

AD-A171 654

PROTECTION OF ALUMINUM AGAINST CORROSION BY
INCORPORATION OF ORGANIC INHI. (U) MARTIN MARIETTA LABS
BALTIMORE MD G D DAVIS ET AL. JUL 84 MML-TR-85-38(C)

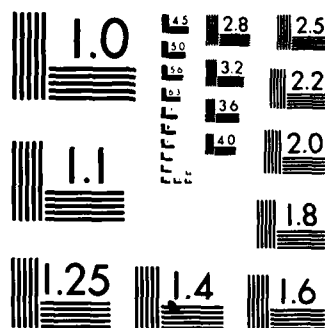
141

UNCLASSIFIED

NO0019-82-C-0439

F/G 11/6

ML



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

AD-A171 654

DTIC ACCESSION NUMBER

LEVEL

PHOTOGRAPH THIS SHEET

MML TR85-38(C)
PROTECTION OF ALUMINUM AGAINST
CORROSION BY INCORPORATION OF
ORGANIC INHIBITORS INTO PAINTS
AND PRIMERS

INVENTORY

FINAL END OF SECOND YEAR

FINAL TECHNICAL REPORT JUNE 85

DOCUMENT IDENTIFICATION

DISTRIBUTION STATEMENT A

Approved for public release
Distribution Unlimited

DISTRIBUTION STATEMENT

ACCESSION FOR

NTIS GRA&I

DTIC TAB

UNANNOUNCED

JUSTIFICATION



BY

DISTRIBUTION /

AVAILABILITY CODES

DIST

AVAIL AND/OR SPECIAL

A-1

DISTRIBUTION STAMP



DTIC
ELECTE
SEP 16 1986

D

DATE ACCESSIONED

DATE RETURNED

REGISTERED OR CERTIFIED NO.

DATE RECEIVED IN DTIC

86 9 15 170

PHOTOGRAPH THIS SHEET AND RETURN TO DTIC-DDAC

De
s 324 D2 1172

MARTIN MARIETTA

MML TR85-38(c)

Martin Marietta
Laboratories

PROTECTION OF ALUMINUM AGAINST
CORROSION BY INCORPORATION OF
ORGANIC INHIBITORS INTO PAINTS
AND PRIMERS

Final End of Second Year
Final Technical Report, June, 1985

APPROVED FOR PUBLIC RELEASE:
DISTRIBUTION UNLIMITED

Prepared for:

Department of the Navy
Naval Air Development Center

Contract No. N00019-82-C-0439

Prepared by:

D.K. Shaffer, L.J. Matienzo, and
G.D. Davis
MARTIN MARIETTA CORPORATION
Martin Marietta Laboratories
1450 South Rolling Road
Baltimore, Maryland 21227

86 9 15 170

AD-A171 654

| REPORT DOCUMENTATION PAGE | | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|---|--|---|
| 1. REPORT NUMBER MML TR85-38(c) | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle) Protection of Aluminum Against Corrosion By Incorporation of Organic Inhibitors into Paints and Primers | 5. TYPE OF REPORT & PERIOD COVERED End-of-Second-Year Final Technical Report | |
| | 6. PERFORMING ORG. REPORT NUMBER MML TR85-38(c) | |
| 7. AUTHOR(s) D.K. Shaffer, L.J. Matienzo, and G.D. Davis | 8. CONTRACT OR GRANT NUMBER(s) N00019-82-C-0439 | |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS Martin Marietta Corporation Martin Marietta Laboratories 1450 South Rolling Road, Balto., MD 21227 | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS | |
| 11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Naval Air Systems Command Washington, DC 20361 | 12. REPORT DATE June, 1985 | |
| | 13. NUMBER OF PAGES | |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Naval Air Development Center Warminster, PA 18974 | 15. SECURITY CLASS. (of this report) Unclassified | |
| | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE | |
| 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. | | |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) N/A | | |
| 18. SUPPLEMENTARY NOTES None | | |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Corrosion, aluminum, corrosion inhibitors, paints, primers, adhesive bonding | | |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Selected organic compounds have been further evaluated on the basis of their ability to inhibit corrosion of aluminum and their bonding compatibility with specified metal-adhesive systems. Organic amino phosphonate and silane inhibitors were applied to sulfuric acid-anodized (SAA) or Forest Products Laboratories (FPL) prepared 7075-T6 aluminum either by adsorption from aqueous solution or by spraying the specified formulation containing the dissolved inhibitor compound. | | |

Wedge test results indicate that in both epoxy-aluminum systems studied, certain organosilanes (i.e. mercapto, epoxy derivatives) tend to both increase the epoxy-metal bond durability and maintain hydration resistance. The results of the salt fog and anodic polarization experiments further suggest that these silane films are effective against localized pitting.

The adsorption of NTMP exhibits a pH-dependent surface coverage, which includes a region characterized by a multilayer of hydrogen-bonded phosphonate molecules. These thick layers are weak and fail to provide good bond durability in a humid environment. NTMP monolayers are protective against hydration and are compatible with a nitrile-modified epoxy adhesive, but not with an epoxy-polyamide primer topcoat.

In contrast, hydrolyzed silane compounds are adsorbed as oligomeric films, and confer corrosion resistance in both hydrating and Cl⁻ environments. These inhibitors can also couple with applied epoxy primer or organosilanes and do not appear to affect the curing process, e.g., % crosslinking, of the polymeric epoxy systems.

TABLE OF CONTENTS

| | <u>Page</u> |
|--|-------------|
| LIST OF FIGURES | iii |
| LIST OF TABLES | v |
| I. INTRODUCTION | 1 |
| II. EXPERIMENTAL | 4 |
| A. STANDARD TECHNIQUES | 4 |
| B. NEW TECHNIQUES | 4 |
| 1. Hydration | 4 |
| 2. Adhesive Bond Durability | 4 |
| 3. Silane Adsorption | 5 |
| 4. Silane Dissolution in Primer | 5 |
| 5. Electrochemical Apparatus | 7 |
| III. RESULTS | 8 |
| A. ALUMINUM SUBSTRATE SURFACE | 8 |
| 1. Sulfuric Acid-Anodized (SAA) Process | 8 |
| 2. Forest Products Laboratory (FPL) Process | 8 |
| B. PROPERTIES OF INHIBITOR COMPOUNDS | 8 |
| 1. Adsorption Studies | 8 |
| a. Phosphonates | 12 |
| b. Silanes | 15 |
| c. Rinsing | 15 |
| 2. Solubility Properties | 15 |
| C. HYDRATION AND CORROSION RESISTANCE EVALUATION | 16 |
| 1. Hydration | 16 |
| 2. Adhesive Bond Durability | 20 |
| 3. Environmental Corrosion Testing | 28 |
| a. Salt-Fog Results | 28 |
| 4. Electrochemical Testing | 31 |
| IV. DISCUSSION | 43 |
| V. CONCLUSION | 46 |
| VI. REFERENCES | 47 |

LIST OF FIGURES

| | <u>Page</u> |
|--|-------------|
| Figure 1. Structure of a sulfuric acid-anodized (SAA) 7075-T6 aluminum surface. | 9 |
| Figure 2. Structure of a Forest Products Laboratories (FPL) 7075-T6 aluminum surface. | 10 |
| Figure 3. Structures of organic corrosion inhibitor compounds. | 11 |
| Figure 4. NTMP coverage as a function of concentration on SAA-prepared 7075-T6 Al surface. | 13 |
| Figure 5. Wedge test (second series) results for inhibitor-treated FPL 7075-T6 Al specimens. | 14 |
| Figure 6. Corrosion results from typical exposed inhibitor-treated FPL 7075-T6 test specimens. | 19 |
| Figure 7. Hydration results from typical exposed inhibitor-treated FPL 7075-T6 test specimens. | 22 |
| Figure 8. Wedge test method used to determine adhesive bond durability. | 23 |
| Figure 9. XPS surface analysis results for debonded SAA 7075-T6 Al wedge test specimens. | 25 |
| Figure 10. Wedge test (first series) results for inhibitor-treated FPL 7075-T6 Al specimens. | 26 |
| Figure 11. Wedge test (second series) results for inhibitor-treated FPL7075-76 Al specimens. | 27 |
| Figure 12. Wedge test results for primed FPL 7075-T6 Al specimens. | 29 |
| Figure 13. FPL 7075-T6 Al exposed to standard NaCl salt fog environment; (a) untreated and (b) primed (unpigmented) control specimens. | 33 |
| Figure 14. FPL 7075-T6 Al specimens exposed to standard NaCl salt fog environment, treated with (a) 100 ppm (pH 5) and (b) 1000 ppm (pH 4) adsorbed NTMP compound. | 34 |

LIST OF FIGURES (Continued)

| | <u>Page</u> |
|--|-------------|
| Figure 15. FPL 7075-T6 Al specimens exposed to standard NaCl salt fog environment, treated with (a) 1000 ppm (adsorbed) and (b) 5000 ppm (sprayed) M-8500 compound. | 35 |
| Figure 16. FPL 7075-T6 Al specimens exposed to NaCl salt fog environment, treated with (a) 5000 ppm G-6720 (sprayed) and (b) 5000 ppm DPBP (sprayed) compounds. | 36 |
| Figure 17. FPL 7075-T6 Al exposed to SO ₂ salt fog; (a) untreated and (b) primed (unpigmented) control specimens. | 37 |
| Figure 18. FPL 7075-T6 Al specimens exposed to SO ₂ salt fog, treated with (a) 100 ppm (pH 5) and (b) 1000 ppm (pH 4) adsorbed NTMP compound. | 38 |
| Figure 19. FPL 7075-T6 Al specimens exposed to SO ₂ salt fog, treated with (a) 1000 ppm (adsorbed) and (b) 5000 ppm (sprayed) M-8500 compound. | 39 |
| Figure 20. FPL 7075-T6 Al specimens exposed to SO ₂ salt fog, treated with (a) 5000 ppm G-6720 (sprayed) and (b) 5000 ppm DPBP (sprayed) compounds. | 40 |
| Figure 21. Electrochemical test results for two different inhibitor compounds in 0.1 N Na ₂ SO ₄ electrolyte with added KC and inhibitors. The working electrode is polished 7075-T6 aluminum. | 41 |

LIST OF TABLES

| | <u>Page</u> |
|---|-------------|
| Table I. Silane adsorption on FPL 7075-T6 surfaces determined by XPS analysis | 6 |
| Table II. Solubilities of inhibitor compounds in epoxy system | 17 |
| Table III. Corrosion resistance rating for FPL - adsorbed inhibitors (2.5, 5, 14 hr) | 18 |
| Table IV. Corrosion resistance rating for FPL - adsorbed inhibitors (1, 2, 16 hr) | 21 |
| Table V. XPS Failure analysis results for wedge test with primed FPL 7075-T6 specimens. | 30 |
| Table VI. Environmental Salt-Fog Results | 32 |

I. INTRODUCTION

Three phases of the proposed work plan were completed during the first year of the contract (2/1/83 - 1/31/84). First, the specified surface of the 7075-T6 Al alloy (sulfuric acid-anodized, or SAA) was characterized morphologically and chemically as a prerequisite to subsequent adsorption and bonding studies. Secondly, the designated two-component epoxy primer system was likewise characterized, with respect to composition and actual curing kinetics, at different temperatures. Finally, the optimal conditions for adsorption of phosphonate inhibitor compounds onto the SAA surface were determined.

In addition to these developments, the phosphonates were (a) added to the epoxy primer in several different forms and to the SAA oxide surface by adsorption and spraying, (b) studied with respect to their effect on the curing chemistry and kinetics of the epoxy resin, and (c) analyzed by four surface techniques after substrate adsorption and/or delivery into the primer, all according to the original work schedule. Screening of the silane compounds with respect to their surface adsorption properties was also initiated prior to the end of 1983. Adhesion and corrosion testing of phosphonate-treated SAA specimens, not scheduled to begin until February 1984, was accomplished not only for those compounds, but also for several organosilanes. Specifically, two wedge tests (adhesive bond durability) and one salt fog (long-term environmental corrosion) test were completed, to evaluate a total of fifteen different phosphonate and silane formulations relative to the respective SAA controls. In unscheduled investigations, four inhibitors were evaluated in the environmental atmosphere relative to pigmented and unpigmented chromic oxide (i.e., chromate conversion-coated) 7075-T6 surfaces, under the direction of NADC.

Of all of the candidate inhibitors evaluated during the first year, several compounds showed promise as hydration inhibitors and adhesion

promoters in the wedge tests, relative to the untreated SAA controls. However, the determination of these findings often required detailed surface analysis (XPS, SEM) of the debonded surfaces to confirm the mode of failure. Evaluation of the inhibitors in a standard salt-fog environment left all of the test specimens, including the SAA-protected controls, completely unaffected after 1200 hours. This was an unexpected result, even though the SAA 7075-T6 surface had not been previously characterized with respect to environmental corrosion or adhesive bonding compatibility. Thus, a modification of the substrate surface was required to effectively evaluate the inhibitor compounds. Corrosion testing with the thinner FPL (Forest Products Laboratories) oxide surface began for phosphonates (exactly on schedule) and for sulfonates and silanes (three quarters ahead of schedule) in May 1984.

Corrosion testing with the FPL specimens furnished satisfactory comparative data for the inhibitors as hydration retardants and adhesion promoters. A considerable background of experience with FPL surfaces furnished necessary information with respect to their chemistry, morphology and specific conditions for the adsorption of phosphonate (and by analogy sulfonate) compounds. In contrast, the adsorption behavior of the neutral and unionized organosilanes remained to be determined prior to their application to the aluminum substrate. With the addition of methods to study initial humidity exposure effects and sensitive electrochemical processes, a test regimen to evaluate the hydration resistance, adhesive bond durability and environmental (salt-fog, electrochemical) properties of candidate inhibitors was established and implemented.

The development of a new means of delivering the inhibitor compounds into the primer-metal system was sought to complement the solution adsorption process. Ideally, if selected compounds could be made miscible with the primer formulation, they could be applied by direct spraying onto the substrate surface. Following completion of the screening regimen for the

sulfonate and silane candidates, subsequent confirmatory testing of target inhibitors would constitute the necessary preparation of the final protective primer-inhibitor formulation. These considerations represented the primary development goals entering the second year.

II. EXPERIMENTAL

A. STANDARD TECHNIQUES

Analytical techniques (SEM, XPS, AES, FTIR, DSC) for the morphological and chemical characterization of metal substrates and epoxy formulations, adsorption and dissolution of organophosphonate inhibitor compounds, and testing by hydration, salt-fog and wedge test methods have been previously reported.⁽¹⁾

B. NEW TECHNIQUES

The following experimental methods are described:

1. Hydration

An evaluation of the inhibitor compounds as antihydration agents was conducted for the FPL-prepared 7075-T6 Al coupons. The test is designed to evaluate only the adsorbed compound as a corrosion inhibitor, as no protective coating is subsequently applied to the surface. The treated test specimens were exposed in a humid environment (95% r.h., 65°C) for 2.5, 5 and 14 hour time periods. Visual examination of the coupons surfaces permitted an evaluation based on the extent of deterioration (discoloration) of the alloy.

2. Adhesive Bond Durability

The evaluation of hydration inhibitor compounds by the wedge test was carried out for SAA- and FPL-treated Al specimens. The test involves bonding the inhibitor-adsorbed panels together with an epoxy-based structural adhesive, driving a standard wedge to induce a stress normal to the primer-xide interface, and subjecting the system to a controlled humid environment

to accelerate crack propagation. The ability of the test compounds to inhibit hydration of the oxide is determined by plotting crack length vs. time relative to the untreated FPL control case, and by performing surface analysis on the debonded surfaces to obtain the mode of failure.

3. Silane Adsorption

FPL- or SAA-prepared test coupons and panels were immersed in an aqueous (or aqueous/alcoholic) silane inhibitor solution at room temperature for times ranging from 40 min to 4 hr (cf. average immersion time for phosphonates of 30 min). Silane concentrations of 1000 and 5000 ppm and solutions of pH = 4 or 7 were employed for these studies (see Table I). An average immersion time of 40 min. was observed in subsequent freshly-prepared inhibitor solutions. The specimens were then rinsed in distilled, deionized water and dried by forced ambient air. Coverage levels of adsorbed silane inhibitors were determined from the Si/Al atomic concentration ratios by XPS surface analysis.

4. Silane Dissolution in Primer

Selected organosilane compounds (liquids) were added directly to a 1:1:1 mixture of the epoxy formulation A (Shell EPON 1001-T75 epoxy resin: EGMEE 16.4%, MEK 4.1%, SrCrO_4 12.0%, TiO_2 2.3%, MgSiO_3 5.5%, SiO_2 talc 2.9%) plus B (Versamid 115 polyamide curing resin: isopropanol 24.5%, toluene 6.6%) and solvent (MIL-T-81772) immediately prior to spraying onto prepared 7075-T6 Al specimens. The final inhibitor concentrations were either 1000 or 5000 ppm (v:v).

Table I

Silane Adsorption onto FPL 7075-T6 Surfaces

| <u>Silane</u> | <u>Concentration (ppm)</u> | <u>Solvent System</u> | <u>pH</u> | <u>Immersion Time</u> | <u>Si/Al</u> |
|---------------|--------------------------------|-----------------------------------|-----------|---------------------------|--------------|
| P-810 | 1000 | W (water) | 4 | 40 min | 0.04 |
| P-810 | 1000 | W (water) | 7 | 40 min | 0.07 |
| P-810 | 1000 | M/W (meth- anol-water, 1:1) | 4 | 40 min | 0.076 |
| P-810 | 1000 | W | 4 | 4 hr | 0.10 |
| G-6720 | 1000 | W | 4 | 40 min | 0.148 |
| G-6720 | 1000 | W | 7 | 40 min | 0.083 |
| G-6720 | 1000 | M/W | 4 | 40 min | 0.127 |
| G-6720 | 1000 | W | 4 | 4 hr | 0.158 |
| A-800 | 1000 | W | 4 | 40 min | 0.364 |
| A-800 | 1000 | W | 7 | 40 min | 0.460 |
| A-800 | 1000 | M/W | 4 | 40 min | 0.330 |

5. Electrochemical Apparatus

Electrochemical behavior of the 7075-T6 alloy was analyzed by anodically polarizing specimens with a PAR Model 273 potentiostat/galvanostat to assess the ability of the inhibitors to promote passivation in chloride-containing electrolytes. The Al surfaces were polished to a 4000-grit finish with SiC paper, degreased with a solvent, and washed in an alkaline detergent solution. Each sample to be polarized was then placed for 30 min in deaerated electrolytic solutions containing chloride (0.002 N KCl) as the aggressive ion species and 0.1 N Na_2SO_4 to minimize the impedance of the electrolyte. Inhibitors were added to the solution in concentrations known to provide the optimum surface coverage.⁽²⁾ This method of inhibitor incorporation was chosen over preadsorbed specimens to avoid possible dissolution of the adsorbed ionic inhibitors during the polarization period. Each sample was scanned anodically at a rate of 0.5 mV/s.

III. RESULTS

A. ALUMINUM SUBSTRATE SURFACE

1. Sulfuric Acid-Anodized (SAA) Process

The complete morphological characterization of the SAA-prepared 7075-T6 Al surface culminated in the production of an isometric scale drawing, shown in Fig. 1. The porous oxide consists of a thin barrier layer under a dense network of closely-packed pore cells (200-600 Å in diameter with pores 100-300 Å wide). The cells generally are separated by relatively wide crevices.

2. Forest Products Laboratory (FPL) Process

The Al surface was subsequently prepared using the FPL ($\text{Na}_2\text{Cr}_2\text{O}_7$ - H_2SO_4) process to produce a much thinner (~ 400 Å) oxide than corresponding SAA-treated specimens, allowing the inhibitor candidates to be evaluated in a reasonable time frame with respect to environmental exposure experiments. The FPL surface, which has been extensively characterized at Martin Marietta Laboratories, is shown isometrically in Fig. 2.

B. PROPERTIES OF INHIBITOR COMPOUNDS

1. Adsorption Studies

The structures of pertinent phosphonate and silane inhibitor compounds are shown in Fig. 3.

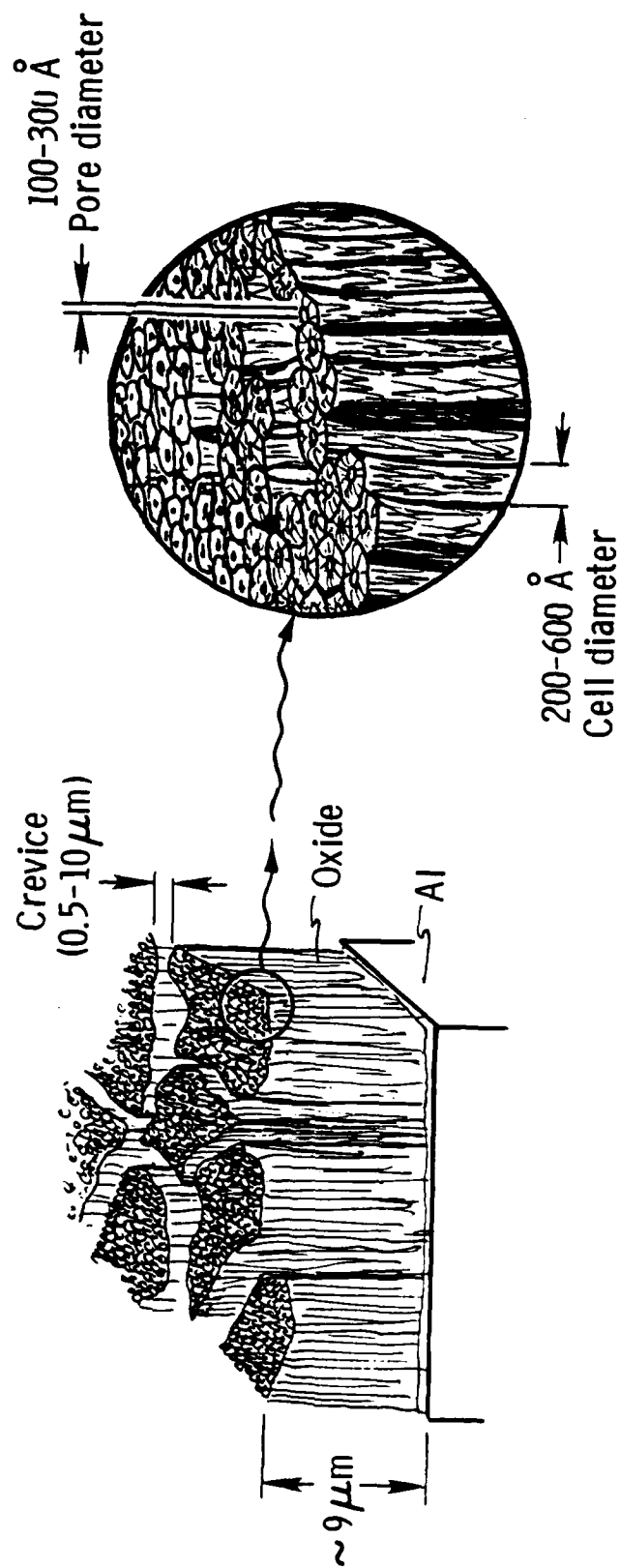


Figure 1. Structure of a sulfuric acid-anodized (SAA) 7075-T6 aluminum surface.

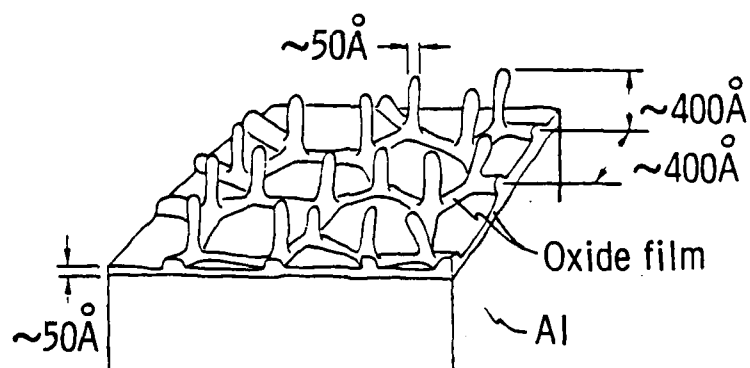
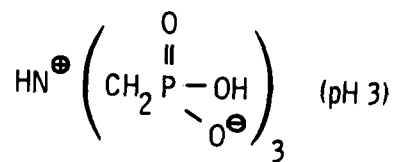


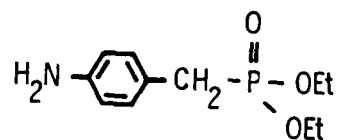
Figure 2. Structure of a Forest Products Laboratories (FPL) 7075-T6 aluminum surface.

Phosphonates

NTMP

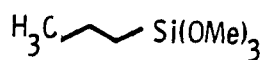


DABP

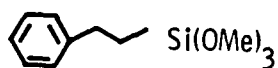


Silanes

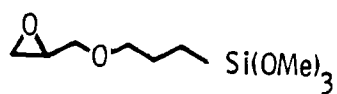
P-810



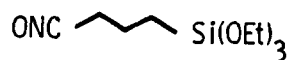
P-113



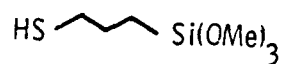
G-6720



I-7840



M-8500



A-800

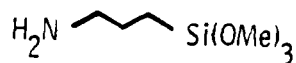


Figure 3. Structures of organic corrosion inhibitor compounds.

a. Phosphonates

Among the two classes of ionic inhibitor candidates, the phosphonates have been the most thoroughly studied, according to the original proposed work plan. With an SAA Al substrate, NTMP coverage (P/Al ratio), as monitored over a wide concentration range, is shown in Fig. 4. Close examination of the curve in the low NTMP concentration end (Fig. 5) revealed a region of constant concentration between 10 and 100 ppm NTMP followed by an adsorption maximum in the 1000 ppm region. This type of multilayer coverage had not been previously observed for a well-rinsed oxidized Al surface treated at room temperature.

The relationship between the level of NTMP coverage and the solution pH on a SAA-prepared surface initially indicated that the inhibitor thickness grew as the pH was increased up to around pH 5, after which it remained constant. Individual data points at pH 3 indicated a particularly high coverage level. A close examination of the coverage behavior in the pH 2-4 range revealed an adsorption maximum of NTMP with a SAA surface.

The adsorption properties of additional phosphonate inhibitors were determined for the SAA surface.⁽¹⁾ The free acid phosphonates (NTMP, PPA) are readily adsorbed, while the phosphonate ester (DABP) is not strongly adsorbed at the unadjusted solution pH. Phosphonate and sulfonate compounds were also adsorbed onto the modified FPL surface under different conditions of concentration, pH, solvent system and adsorption time. While optimal FPL adsorption conditions for the ionizable phosphonate and sulfonate compounds closely paralleled conditions determined for the SAA system, such adsorption parameters for the silane compounds were not previously known.

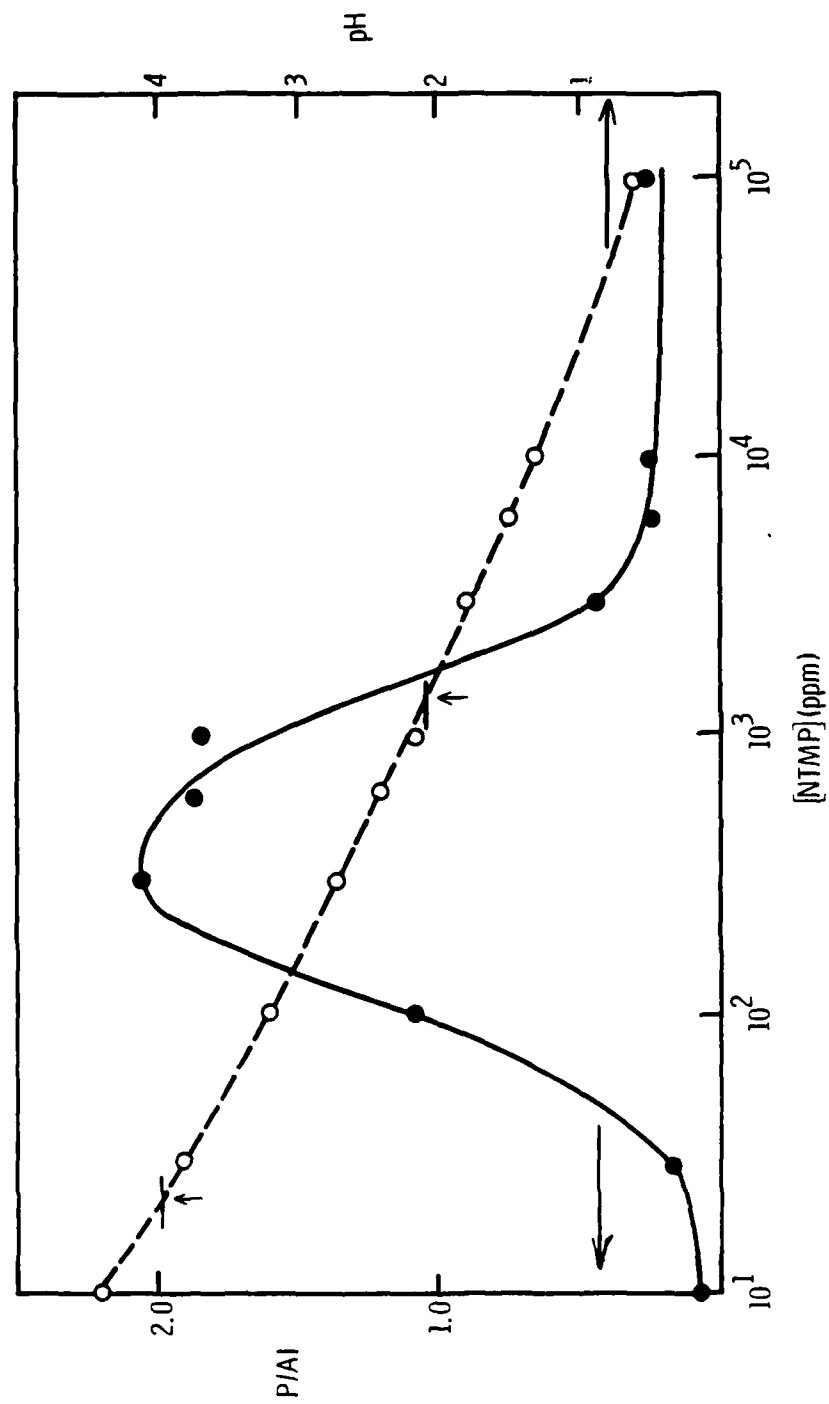


Figure 4. NTMP coverage as a function of concentration on SAA-prepared 7075-T6 Al surface.

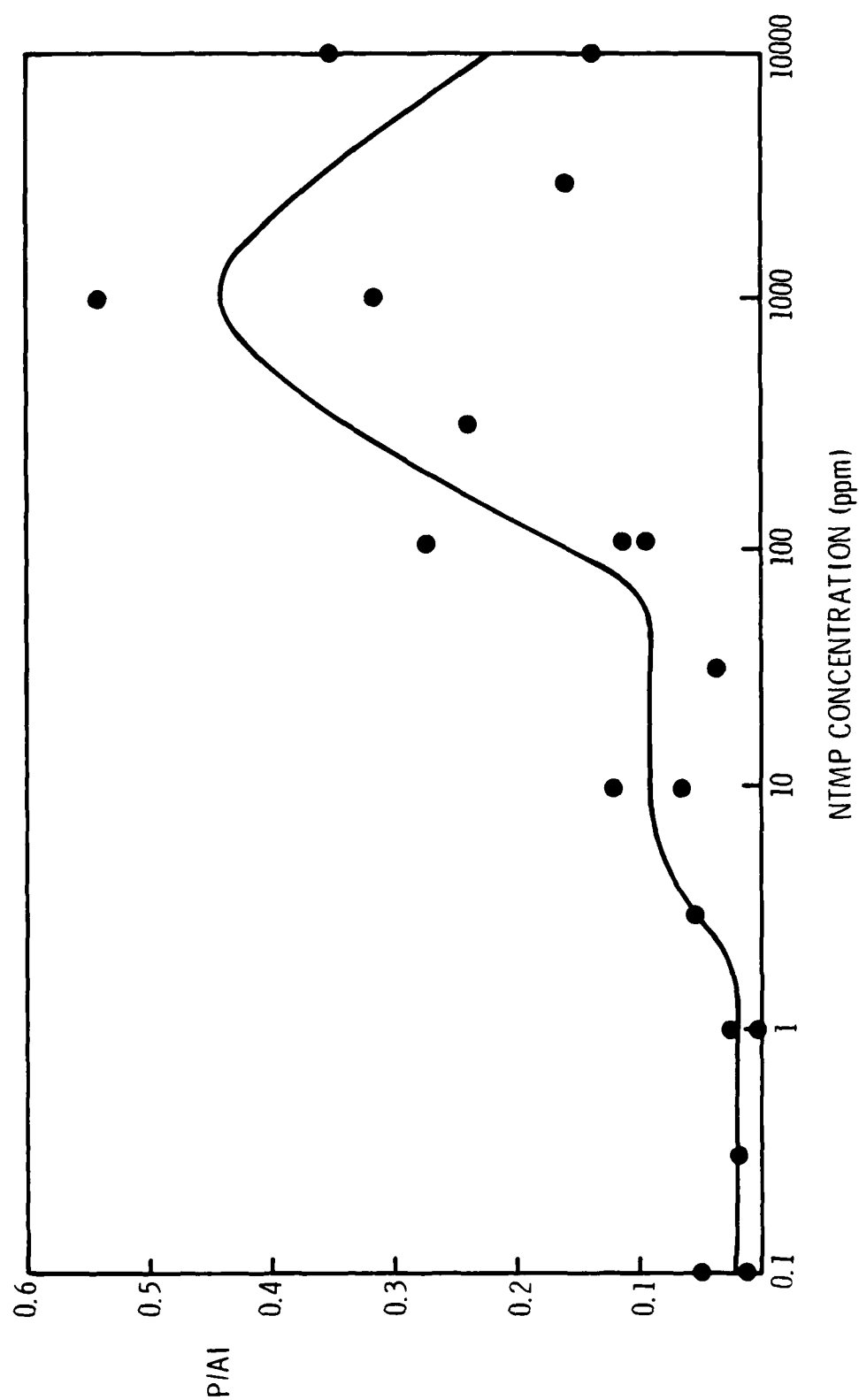


Figure 5. P/Al vs. pH (adjusted) for 7075-T6 Al coupons immersed in 100 ppm NTMP (40 min); surface preparations by SAA (o---o) and FPL (o---o) treatments.

b. Silanes

Silane compounds were adsorbed onto FPL-prepared Al surfaces. Coverage levels were determined using X-ray photoelectron spectroscopy (XPS) Si/Al ratios. The results are presented in Table I. At the 1000-ppm concentration level, neutral silanes (propyl and epoxy derivatives) were best adsorbed at pH 4. For the amino derivative, slightly more of the silane was adsorbed at pH 7. The optimal conditions of solvent system (water or methanol/water, 1:1) and immersion time (40 min or 4 hr) depend on the individual inhibitor systems and are generally similar.

c. Rinsing

Finally, the importance of the solvent rinse following inhibitor adsorption must be noted. The higher NTMP coverages observed at 1000 ppm resulting from rinsing with anhydrous ethanol ($P/Al=2.0$) in place of water, ($P/Al=0.45$) indicates that water can remove some of the adsorbed ionic phosphonate compound. Similarly, rinsing of adsorbed silanes with ethanol will remove those (silane) inhibitors, which are more compatible with the less polar ethanol than with water. In general, it is recommended that surfaces treated with phosphonates and sulfonates be rinsed with ethanol, while silane-adsorbed surfaces are adequately cleaned by aqueous rinsing.

2. Solubility Properties

Initial attempts to add inhibitor compounds to the two-component epoxy resin system resulted in solubilization of three phosphonates (PPA, DABP, DRAP) in isopropanol, the major solvent constituent of the B component. Subsequently, PPA and DABP were applied to corrosion salt-fog test panels by spraying the inhibitor-containing primer formulation, after the addition of these compounds in an isopropanol solution. The more polar phosphonates

(NTMP, CRP), on the other hand, were only sparingly soluble in the solvent, and could not be delivered via spraying. Although a 5% "mull" suspension of solid NTMP in the epoxy resin had no apparent effect on the normal curing process,⁽¹⁾ its subsequent effectiveness as a corrosion inhibitor at the substrate surface was not determined.

In more recent work, twenty inhibitor compounds were added directly to the A component of the epoxy-polyamide system prior to mixing with the B component. At least 5% (v/v for liquids, w/v for solids) of each compound was added. The results, presented in Table II, indicated that the majority of the silane compounds are readily miscible with both the A component and the mixed A + B system. They did not have any apparent effect on the epoxy curing kinetics or the appearance of the final cured resin. These findings contrast sharply with those for the solid phosphonate compounds, which proved insoluble in the individual component, mixed and cured formulations.

C. HYDRATION AND CORROSION RESISTANCE EVALUATION

1. Hydration

The hydration results are presented in Table III, and corresponding exposed specimens from the test are shown in Fig. 6. The results indicated that the M-8500 (mercaptopropyl trimethoxysilane) compound performed better than all of the inhibitors and the FPL control with respect to both short and long-term corrosion (hydration) resistance. While several other systems demonstrated good short-term resistance, only the CRP (creatine phosphate) compound provided moderate protection after the 14-hr exposure period. Concentration and pH conditions were also monitored with some compounds, and no significant differences in appearance were observed among the test specimens.

TABLE IISolubilities of Inhibitor Compounds in Epoxy System

| <u>Compound</u> | <u>Solubility in A Component</u> | <u>Appearance of Final Cured Resin</u> |
|-----------------|----------------------------------|--|
| Control | Readily soluble (Clear) | Clear |
| T-2900 | Readily soluble (Clear) | Clear |
| DABP | Readily soluble (Clear) | Clear |
| Z-6040 | Readily soluble (Clear) | Clear |
| M-8500 | Readily soluble (Clear) | Clear |
| P-113 | Readily soluble (Clear) | Clear |
| P-810 | Readily soluble (Clear) | Clear |
| E-6250 | Readily soluble (Clear) | Clear |
| G-6720 | Readily soluble (Clear) | Clear |
| P-330 | Readily soluble (Clear) | Slightly cloudy |
| V-4917 | Readily soluble (Clear) | Slightly cloudy |
| A-725 | Readily soluble (Brown) | Clear (Brown) |
| D-6150 | Slightly cloudy | Clear |
| DPAP | Slightly cloudy | Clear |
| I-7840 | Slightly cloudy | Slightly cloudy, no |
| PPA | Slightly cloudy | Clear (slight ppt) |
| OSA | Clear (slight ppt) | Ppt |
| A-800 | Cloudy | Ppt |
| T-2910 | Cloudy | Ppt |
| VTMP (S) | Cloudy (w/ppt) | Ppt |
| VTMP (N) | Cloudy (w/ppt) | Ppt |
| CRP | Fine suspension | Ppt |
| DPAS | Fine suspension | Ppt |

TABLE III

Corrosion Resistance Rating for FPL-Adsorbed Inhibitors

Corrosion Rating *

| <u>Type</u> | <u>No.</u> | <u>Specimen</u> | <u>2.5 hr</u> | <u>5 hr</u> | <u>14 hr</u> |
|---------------|------------|--------------------|---------------|-------------|--------------|
| Control | 0 | FLP | P | P | P |
| Phosphonates | 1 | NTMP | G | F | F-P |
| Phosphonates | 2 | TETAHMPA | G | F | F |
| Phosphonates | 3 | n-BuNBMP | E-G | G-F | F |
| Phosphonates | 4 | EDTMPA | G | G-F | F |
| Phosphonates | 5 | DABP | F | F | F-P |
| Phosphonates | 6 | DPAP | F | F-P | P |
| Phosphonates | 7 | PPA | G-F | F | F |
| Phosphonates | 8 | CRP | G | G | G-F |
| Sulfonates | 9 | OSA | P | P | P |
| Sulfonates | 10 | PPAS | F | P | P |
| Sulfonates | 11 | PIPES | F-P | P | P |
| Silanes | 12 | P-310 | G-F | F | P |
| Silanes | 13 | A-300 | F | P | P |
| Silanes | 14 | M-3500 | E | E | E |
| Silanes | 15 | G-6720 | F | F-P | P |
| Silanes | 16 | I-7840 | F | F-P | P |
| Concentration | 17 | NTMP (10^4 ppm) | G-F | F | F-P |
| Concentration | 18 | NTMP (10^3 ppm) | G | G-F | F-P |
| Concentration | 19 | NTMP (10^2 ppm) | G | F | F |
| pH | 20 | NTMP (pH 2) | G-F | P | P |
| pH | 21 | NTMP (pH 3.5) | G-F | F | P |
| pH | 22 | NTMP (pH 5) | G-F | F | P |
| pH | 23 | NTMP (pH 7) | G-F | P | P |

* Rating System: E = excellent, G = good, F = fair, P = poor

FPL CORROSION RESULTS

| <u>Sample</u> | <u>Exposure Time*</u> | | | <u>Structure</u> |
|---------------|-----------------------|-------------|--------------|--|
| | <u>2.5 hr</u> | <u>5 hr</u> | <u>14 hr</u> | |
| FPL | | | | |
| NTMP | | | | $\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_3$ |
| PPAS | | | | |
| A-800 | | | | $\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OMe})_3$ |
| M-8500 | | | | $\text{HS}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OEt})_3$ |

*Exposure time in Blue M Humidity Chamber (95% r.h., 65°C)

Figure 6. Hydration results from typical exposed inhibitor-treated FPL 7075-T6 test specimens.

A second hydration resistance test was conducted to evaluate new inhibitors, over 1, 2 and 16 hour exposure times, adsorbed onto FPL-treated Al coupons. Corrosion (hydration) on the coupon surfaces was again evaluated based on the observed extent of discoloration. These results are shown in Table IV and typical exposed specimens are included in Fig. 7. Several of the treated specimens (i.e., NTMP, CRP, D-6150, G-6720, A-725, M-8500) performed well relative to the untreated FPL control coupons. However, the superior long-term protection of the M-8500 mercaptosilane compound was not as obvious as observed in the first hydration study. Overall, 15 of the 19 inhibitor formulations evaluated provided short-term (0-2 hr) hydration resistance which was clearly superior to that of the untreated FPL control specimens. It should be noted that the hydration test results discussed in Tables III and IV are comparable within each specific test, but not necessarily from test to test.

2. Adhesive Bond Durability

The hydration of bonded aluminum structures (wedge test) ultimately leads to deadhesion of the joints, including the types produced by commercial aerospace bonding processes. Adhesive-containing primer formulations (e.g. epoxy-polyamide) are readily evaluated by this method. The test, illustrated in Fig. 8, specifically evaluates the bond strength of the adherend-adhesive system, i.e., the effectiveness of the coating which actually protects the metal surface from the outside corrosive environment.

The first two wedge tests indicated good bond durability performance by low concentration (2-100 ppm) NTMP, intermediate concentration (100-500 ppm) PPA, Z-6040 and A-800 and high concentration (5000 ppm or 0.5%) Z-6040 adsorption treatments on SAA-prepared 7075-T6 Al surfaces. While the crack length-time data only indicated adhesion properties equivalent to those of the

TABLE IV

Corrosion (Hydration) Resistance for Exposed
Inhibitor-Treated FPL Specimens

| <u>Type</u> | <u>No.</u> | <u>Inhibitors</u> | <u>[ppm]</u> | <u>Initial pH</u> | <u>Corrosion Rating *</u> | | |
|-------------|------------|-------------------|--------------|-------------------|---------------------------|-------------|--------------|
| | | | | | <u>1 hr</u> | <u>2 hr</u> | <u>16 hr</u> |
| Control | 0 | FPL | --- | --- | P | P | P |
| Control | 00 | SAA (0 min)** | --- | --- | P | P | P |
| Control | 00A | SAA (2 min) | --- | --- | E | E | G |
| Control | 00B | SAA (20 min) | --- | --- | --- | E | EE |
| Phosphonate | 1 | NTMP | 200 | 5 | E | G | F-P |
| Phosphonate | 2 | CRP | 200 | 7 | G | G | F-P |
| Silane | 3 | P- 810 | 1000 | 4 | P | P | P |
| Silane | 4 | P- 330 | 1000 | 4 | P | P | P |
| Silane | 5 | P- 113 | 1000 | 4 | F-P | P | P |
| Silane | 6 | D-6150 | 1000 | 7 | G | F | P |
| Silane | 7 | G-6720 | 1000 | 4 | G | F | P |
| Silane | 8 | E-6250 | 1000 | 4 | P | P | P |
| Silane | 9 | A- 800 | 1000 | 4 | F | P | P |
| Silane | 9A | A- 800 | 1000 | 7 | F-P | P | P |
| Silane | 10 | T-2910 | 1000 | 4 | G-F | F-P | P |
| Silane | 11 | A- 725 | 1000 | 4 | E-G | G-F | P |
| Silane | 12 | T-2900 | 1000 | 4 | G | F-P | P |
| Silane | 13 | V-4917 | 1000 | 4 | F | F-P | P |
| Silane | 14A | M-8500 | 5000 | 4 | E | G-F | P |
| Silane | 14B | M-8500 | 1000 | 4 | E | P | P |
| Silane | 14C | M-8500 | 200 | 4 | E-G | P | P |
| Silane | 14D | M-8500 | 50 | 4 | G | P | P |
| Sulfonate | 15 | DPAS | 1000 | 7 | P | P | P |

* Rating System: E = excellent, G = good, F = fair, P = poor

** Anodization time

HYDRATION TEST RESULTS
























































| Inhibitor | Exposure Time | | | | | | Structure |
|-----------|---|---|---|---|---|---|--|
| | 1 hr | | 2 hr | | 16 hr | | |
| FPL |  |  |  |  |  |  |  |
| NTMP |  |  |  |  |  |  | $\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_3$ |
| CRP |  |  |  |  |  |  | $\text{HOOC}-\text{CH}(\text{CH}_3)-\text{N}(\text{H})-\text{C}(=\text{NH})-\text{N}(\text{H})-\text{P}(=\text{O})(\text{ONa})_2$ |
| D-6150 |  |  |  |  |  |  | $(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2$ |
| T-2910 |  |  |  |  |  |  | $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{H})-\text{CH}_2-\text{CH}_2-\text{N}(\text{H})-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OMe})_3$ |
| A-725 |  |  |  |  |  |  | $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{Si}(\text{OMe})_3$ |
| T-2900 |  |  |  |  |  |  | $\text{H}_2\text{N}-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OMe})_3$ |
| V-4917 |  |  |  |  |  |  | $\text{CH}_2=\text{CH}-\text{Si}(\text{OMe})_3$ |
| M-8500 |  |  |  |  |  |  | $\text{HS}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OMe})_3$ |

Figure 7. Hydration results from typical exposed inhibitor-treated FPL 7075-T6 test specimens.

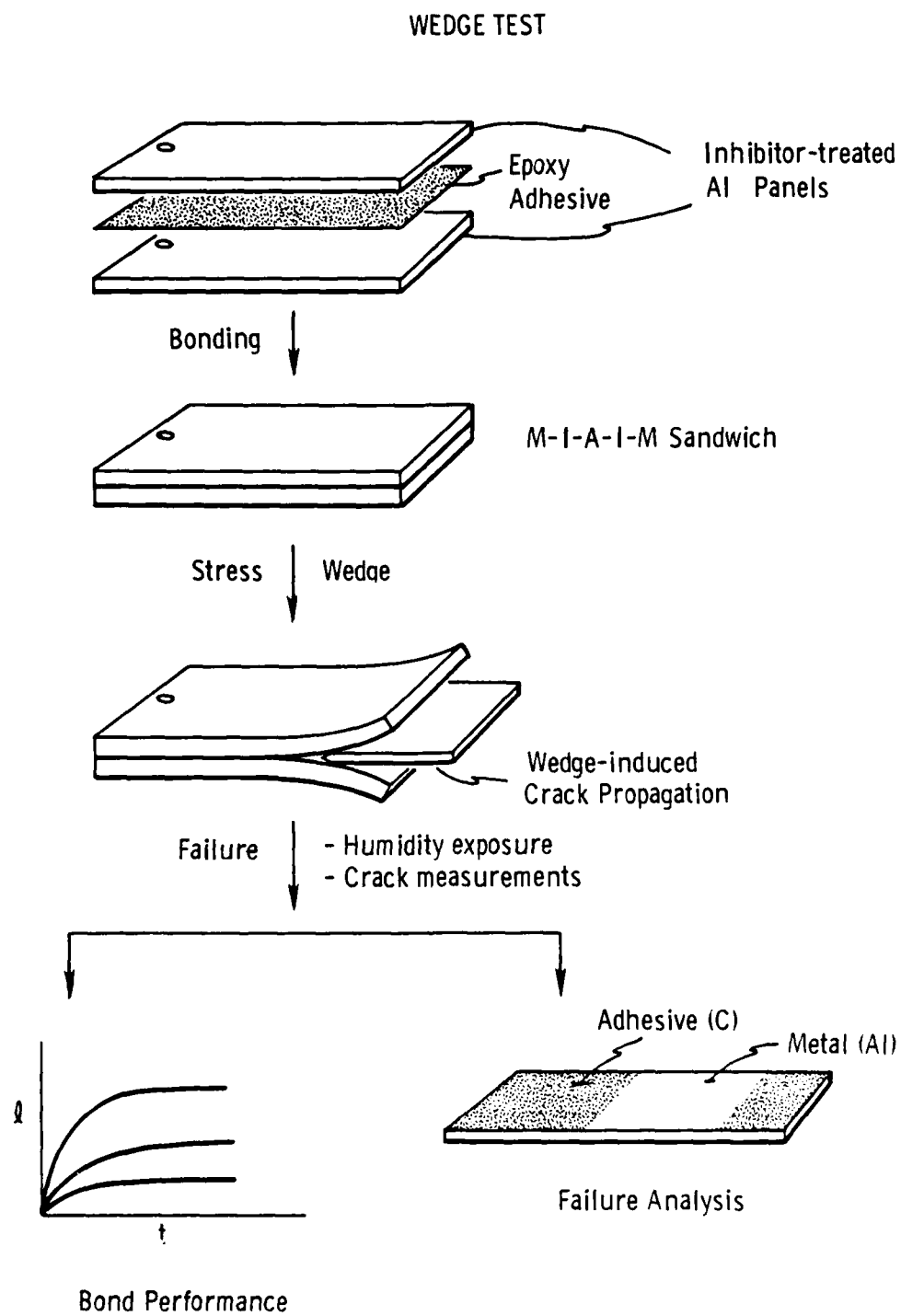


Figure 8. Wedge test method used to determine adhesive bond durability.

SAA control, XPS failure analysis results (Fig. 9) identified the true modes of failure. The SAA control (hydrated oxide on both sides under SEM; high Al and O levels on both sides) failed within the oxide. Examination of the specimen treated with multilayer-forming 5000-ppm NTMP solution (distinct "metal" and "adhesive" sides under SEM; high Al and O, low C levels on "metal" side; high C, low Al and O levels on "adhesive" side) indicated that the failure occurred between the metal and the adhesive (known as an adhesive failure). Although distinct "metal" and "adhesive" sides were apparent upon visual examination of the debonded surfaces treated with 100 ppm NTMP, SEM analysis indicated the presence of an adhesive layer on the "metal" side. XPS analysis showed low Al and O and identical high C levels on both debonded sides, confirming a failure within the adhesive layer (cohesive failure), i.e., the best possible performance in a given adherend-adhesive system. This result is similar to that obtained using a 2024 Al alloy prepared by the phosphoric acid-anodization (PAA) process⁽³⁾ and indicates the importance of monolayer NTMP coverage for good bond durability. SEM and XPS analyses indicated that the epoxysilane system failed by a "mixed mode" process).

A second wedge test was performed to evaluate six silanes and NTMP on the thinner, more sensitive FPL oxide (Fig. 10). The results indicated that four silanes performed better than the FPL control but not as well as NTMP; one silane (an aminopropyl derivative) performed very poorly with respect to the control; and one silane (M-8500, mercaptopropyl derivative) out performed all of the other inhibitor systems, including NTMP and organosilanes containing methyl, phenyl, isocyanate, and epoxide side chains. A second wedge test confirmed these relative bond durability results (Fig. 11). Subsequent XPS analysis of the adsorbed mercaptosilane inhibitor showed high concentrations of Si and S near the surface, with corresponding low Al, the S being primarily in the reduced "inhibitor" (i.e., R-SH) form relative to sulfate ($-\text{SO}_4$)²⁻, resulting from the FPL pretreatment.

A comparison of the relative bond durabilities of different inhibitor-treated specimens (e.g., Figs. 10 and 11) is valid when their respective error

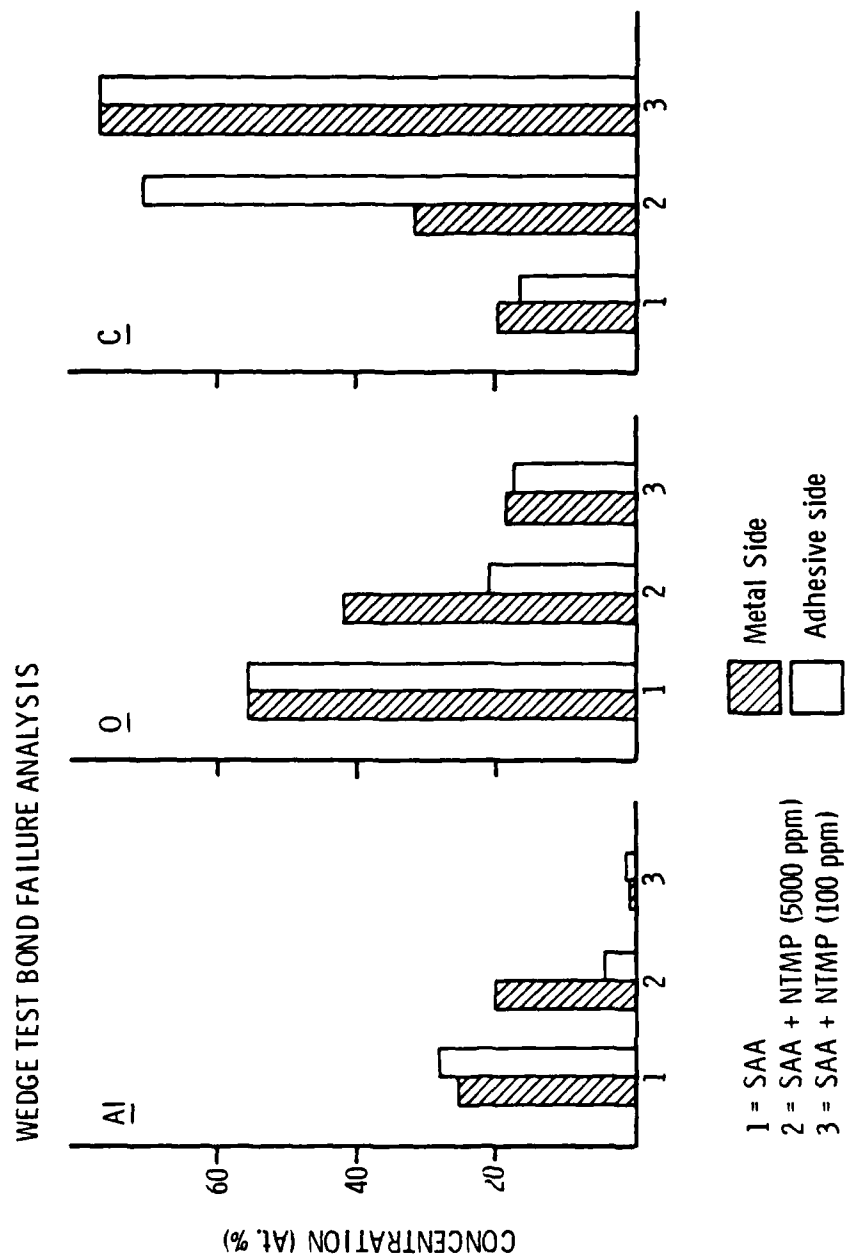


Figure 9. XPS surface analysis results for debonded SAA 7075-T6 Al wedge test specimens.

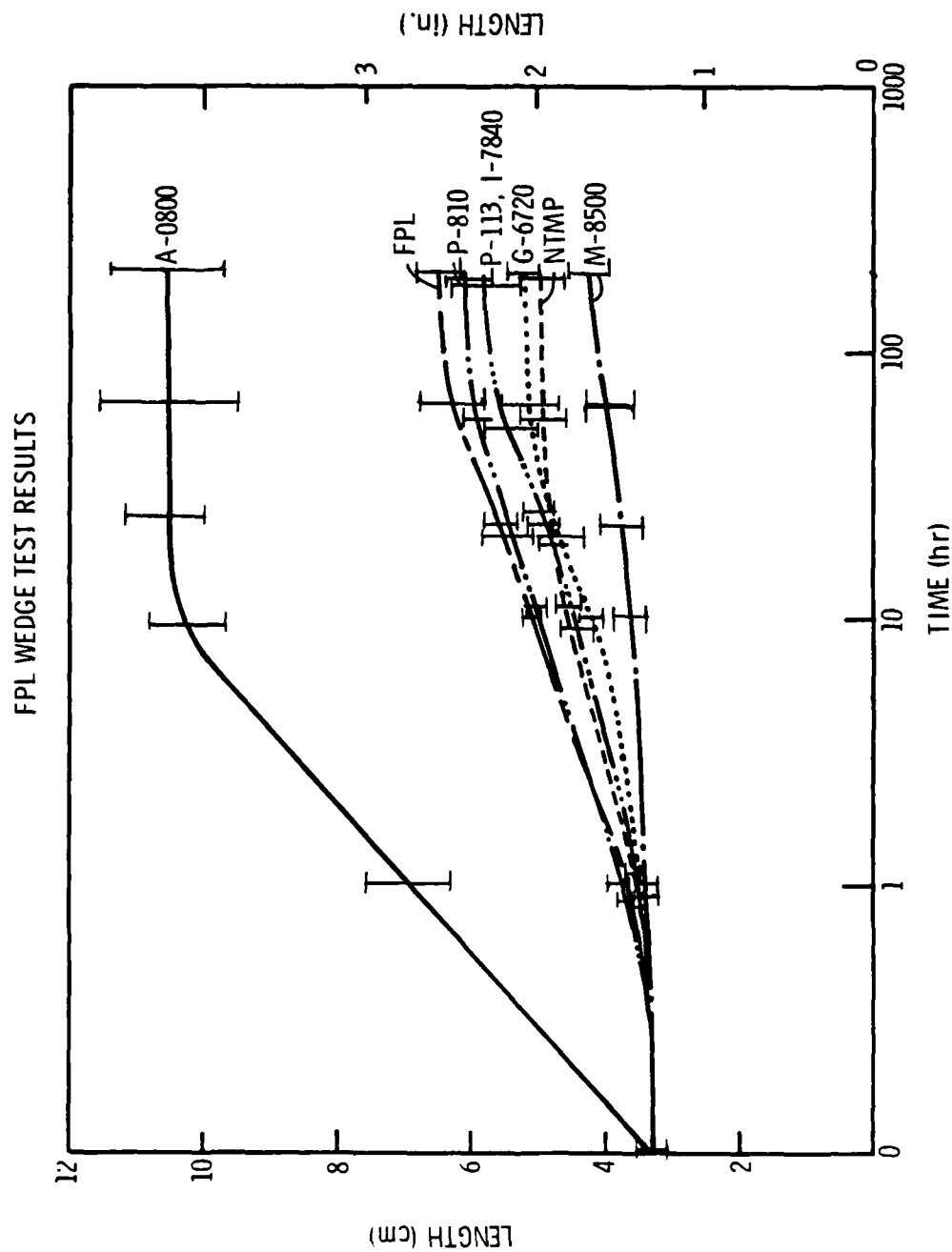


Figure 10. Wedge test (first series) results for inhibitor-treated FPL 7075-T6 Al specimens.

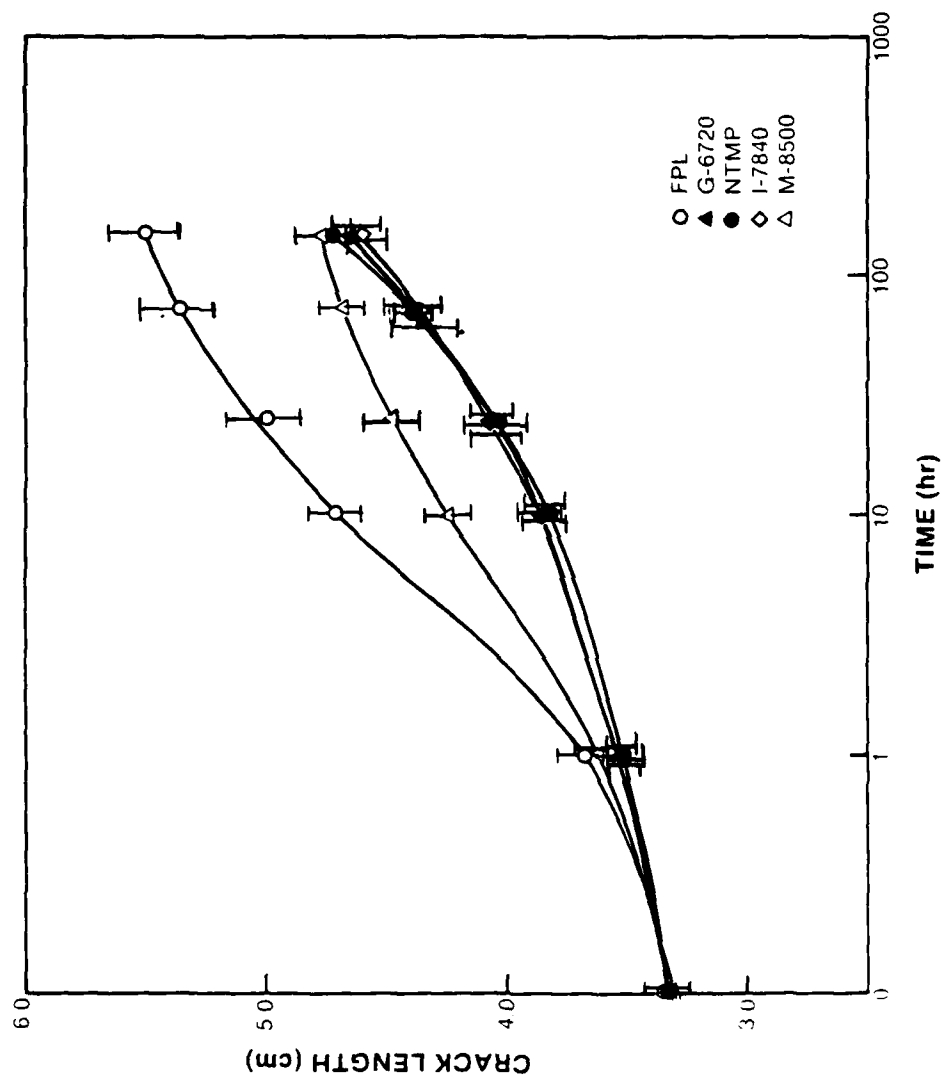


Figure 11. Wedge test (second series) results for inhibitor-treated FPL 7075-T6 Al specimens.

bars do not overlap. The trend of the crack growth orders must also be reproducible from test to test, by far the most common case. However, when wedge test curves for several specimens are virtually colinear, their effectivenesses cannot be distinguished and must be reported as such.

The compatibility of the epoxy-polyamide primer with the nitrile-modified epoxy adhesive facsimile and the aluminum oxide surface was also evaluated by the wedge test, since earlier tests using the primer as the adhesive had failed immediately. As shown in Fig. 12, the addition of the primer improved the overall durability of the aluminum-adhesive system. The application of the mercaptopropylsilane derivative by preadsorption onto the substrate surface effectively maintained or slightly enhanced the bond strength between the primer and the FPL oxide. In contrast, adsorbed NTMP, which preserves the integrity of the (nitrile-modified) adhesive-metal bond, failed to prevent rapid deterioration of the polyamide primer-metal bond. The pigmented primer samples failed immediately as the wedges were being driven.

XPS analysis of the debonded specimens (Table V) provided evidence to explain these results. Using atomic concentrations for the respective metal/adhesive debonded sides, the unprimed (30.0/28.6% Al, 58.2/61% O) and primed (24.6/26.4% Al, 59.4/57.3% O) FPL control and mercaptosilane-treated (27.1/25.0% Al, 54.1/51.3%O) specimens were found to have failed primarily within the oxide, which represented the weakest layer in the system. The higher levels of C on the adhesive side (24.7%) of the NTMP-treated oxide specimens compared to the metal (9.2%) indicated an adhesive failure (i.e., between the oxide and the polyamide primer).

3. Environmental Corrosion Testing

a. Salt-Fog Results

Initial corrosion testing of candidate inhibitors showed that the SAA process is so effective in preventing environmental (i.e., Cl) attack in a

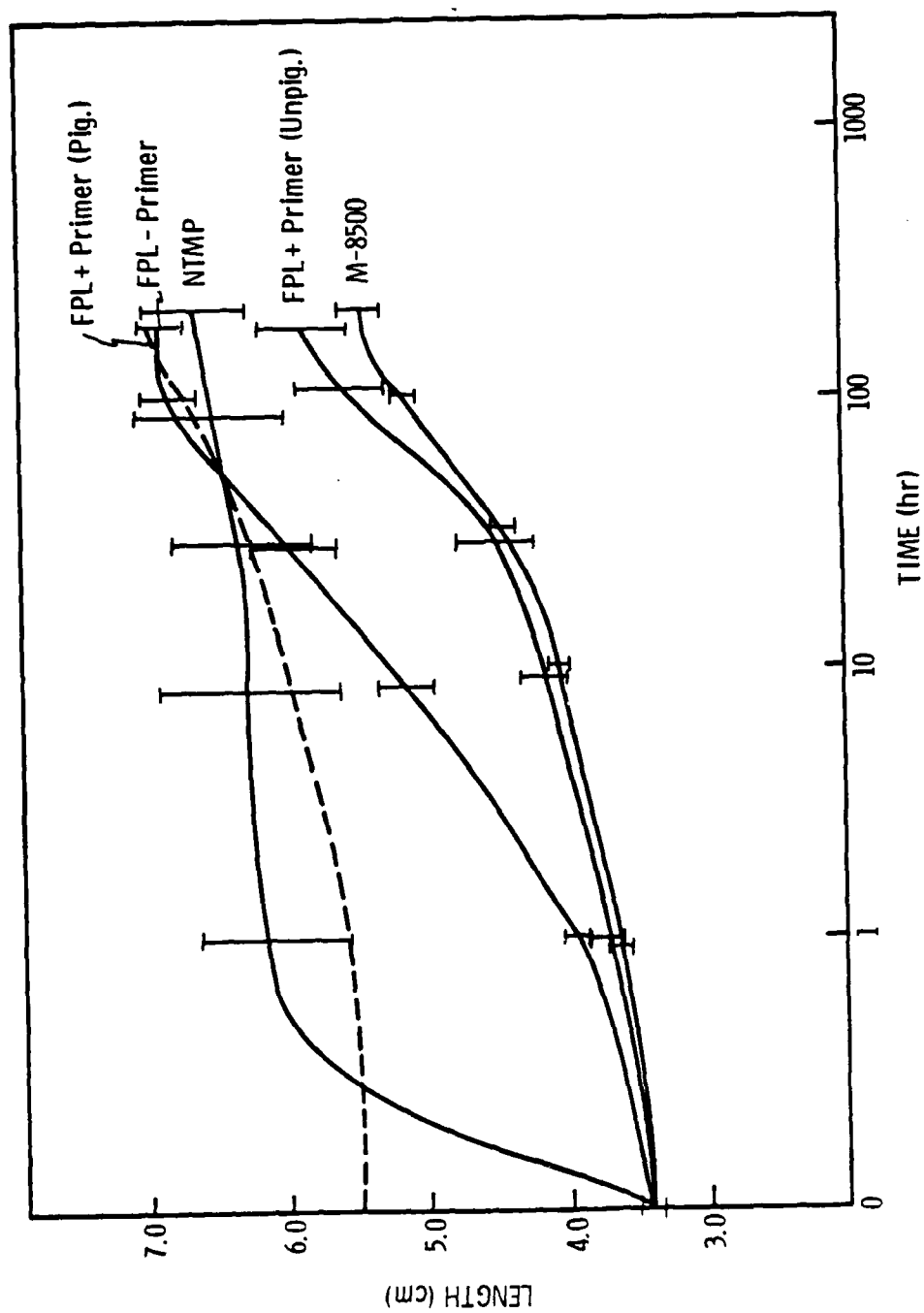


Figure 12. Wedge test results for primed FPL 7075-T6 Al specimens.

TABLE V

XPS Failure Analysis Results for Wedge Test Using Primed FPL Al Specimens (Fig. 12)

| Atomic % | | | | | | | | | |
|----------------------------|----|------|------|---------------------------------------|-----------------|------|------|---------------------------|--------------------|
| "Metal" Side | | | | | "Adhesive" Side | | | | |
| Specimen | Al | O | C | Other | Al | O | C | Other | |
| FPL (- primer) | | 30.0 | 58.2 | 11.8 | ----- | 28.6 | 61.8 | 9.6 | ----- |
| FPL (with pig. primer) | | 2.9 | 30.5 | 45.3 Mg(8.0) N(2.8) Sr(0.27) | Si(10.3) | 2.0 | 28.6 | 47.3 N(6.4) Sr(tr) | Si(9.4) MG(8.5) |
| FPL (with unpig. primer) | | 24.6 | 59.4 | 15.9 | ----- | 26.4 | 57.3 | 16.4 | ----- |
| NTMP (100 ppm adsorbed) | | 32.1 | 58.7 | 9.2 | ----- | 24.7 | 50.6 | 24.7 | ----- |
| M-8500 (1000 ppm adsorbed) | | 27.1 | 54.1 | 18.7 | ----- | 25.0 | 51.3 | 21.1 Cl(tr) Na(tr) | N(2.6) |
| M-8500 (1000 ppm sprayed) | | 30.8 | 58.3 | 10.3 | Cl(0.7) | 26.3 | 52.0 | 14.3 Cl(0.7) Na(tr) | N(6.5) |

standard salt-fog chamber that a practical (<1200 hr) evaluation of the compounds is not possible.⁽¹⁾ No blistering was observed for any of the test specimens, including the SAA control. Non-anodized chromate conversion-coated (CCC) panels generally displayed a poorer resistance to salt-initiated corrosion than the comparable SAA-prepared specimens.

Subsequent standard (ASTM B-117) and accelerated SO₂- salt-fog tests were conducted and the results are presented in Table VI. Representative photographs of the standard (NaCl) and accelerated (SO₂) exposed specimens are shown in Figs. 13-16 and 17-20, respectively.

The NaCl atmosphere attacked the FPL control samples, producing moderate blistering along the scribed regions. All of the treated specimens remained generally free from environmental degradation after 1000 hrs of exposure. In contrast, all inhibitor-treated test panels in the SO₂-containing atmosphere indicated more severe general deterioration than the corresponding NaCl-exposed specimens. In this case, the FPL controls performed somewhat better than the treated panels in both the scribed and unscribed regions. The most severe cases of degradation appeared with the sprayed mercaptosilane (M-8500, 5000ppm) and epoxysilane (G-6720, 5000ppm) treated samples, relative to the FPL control. The intermediate stages of the corroding specimens were not monitored during the 400-hr exposure period.

4. Electrochemical Testing

Potentiodynamic polarization techniques were utilized as a sensitive measure of the ability of silane and phosphonate compounds to inhibit environmental corrosion. The tests involved localized environmental corrosion. The tests involved localized attack on the Al surface by an aggressive (Cl⁻) ion. The results obtained from anodically polarizing polished 7075-T6 Al samples are presented in Fig. 21. For the control electrolyte (0.1N Na₂SO₄, 0.002N KCl, no inhibitor), pitting was observed almost immediately on the surface, and the aluminum showed no evidence of

TABLE VI

Environmental Salt-Fog Results

| Test Type | No. | Specimen | Application | General Appearance | ----Comments*---- | |
|-----------------------------------|-------|------------------|-------------|--------------------|-------------------|-----------|
| | | | | | Scribed | Unscribed |
| Standard(NaCl) (ASTM B-117) | 1-3 | FPL Control | ----- | Fair | MB | ----- |
| Standard | 7-9 | NTMP (100ppm) | Adsorbed | Good | ----- | LB |
| Standard | 13-15 | M-8500 (1000ppm) | Adsorbed | Good | ----- | ----- |
| Standard | 19-21 | M-8500 (1000ppm) | Sprayed | Good | ----- | LB |
| Standard | 25-27 | M-8500 (5000ppm) | Sprayed | Good | ----- | ----- |
| Standard | 31-33 | G-6720 (5000ppm) | Sprayed | Good | ----- | ----- |
| Standard | 37-39 | DPBP (5000ppm) | Sprayed | Good | ----- | ----- |
| ----- | | | | | | |
| Accelerated (SO ₂) | 4-6 | FPL Control | ----- | Fair-Poor | MB | L-MB |
| Accelerated | 10-12 | NTMP (100ppm) | Adsorbed | Poor | M-HB | LB |
| Accelerated | 16-18 | M-8500 (1000ppm) | Adsorbed | Poor | HB | LB |
| Accelerated | 22-24 | M-8500 (1000ppm) | Sprayed | Poor | M-HB | LB |
| Accelerated | 28-30 | M-8500 (5000ppm) | Sprayed | Poorest | HB | HB |
| Accelerated | 34-36 | G-6720 (5000ppm) | Sprayed | Very Poor | M-HB | MB |
| Accelerated | 40-42 | DPBP (5000ppm) | Sprayed | Poor | MB | MB |

*L = LIGHT
M = MODERATE
H = HEAVY
B = BLISTERING

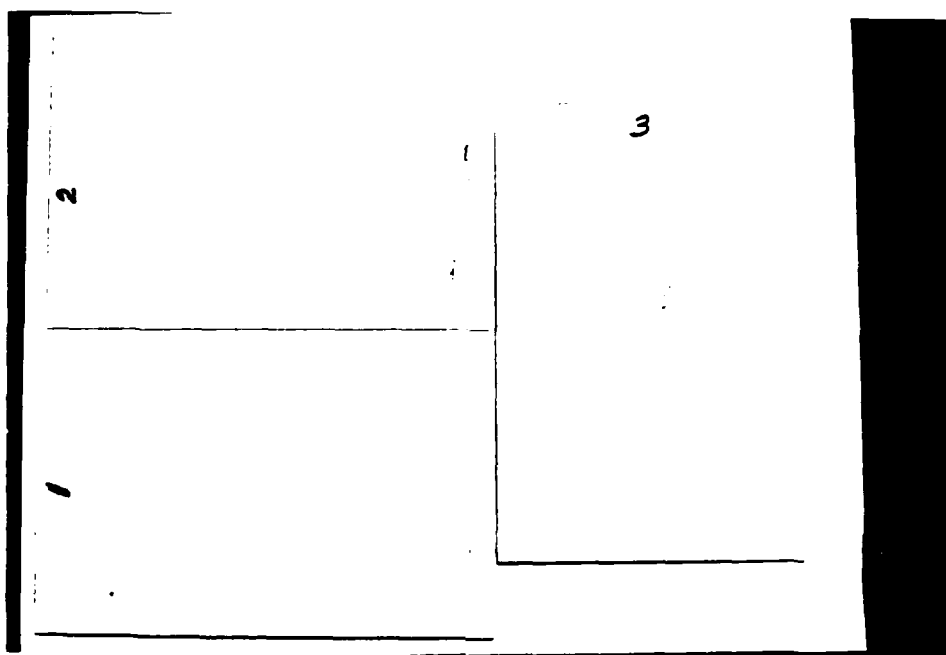
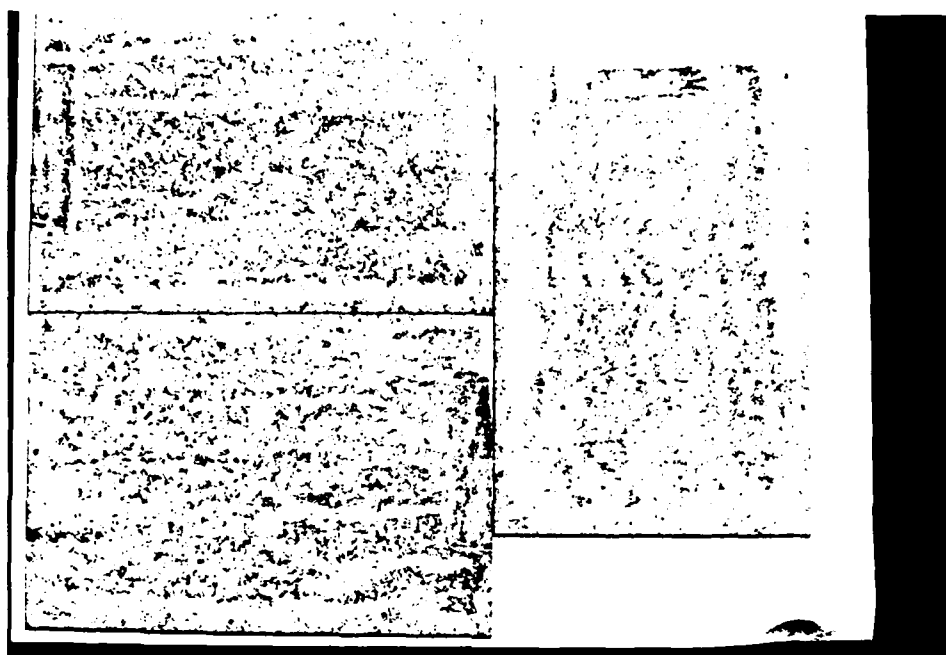


Figure 13. FPL 7075-T6 Al exposed to standard NaCl salt fog environment; (a) untreated and (b) primed (unpigmented) control specimens.

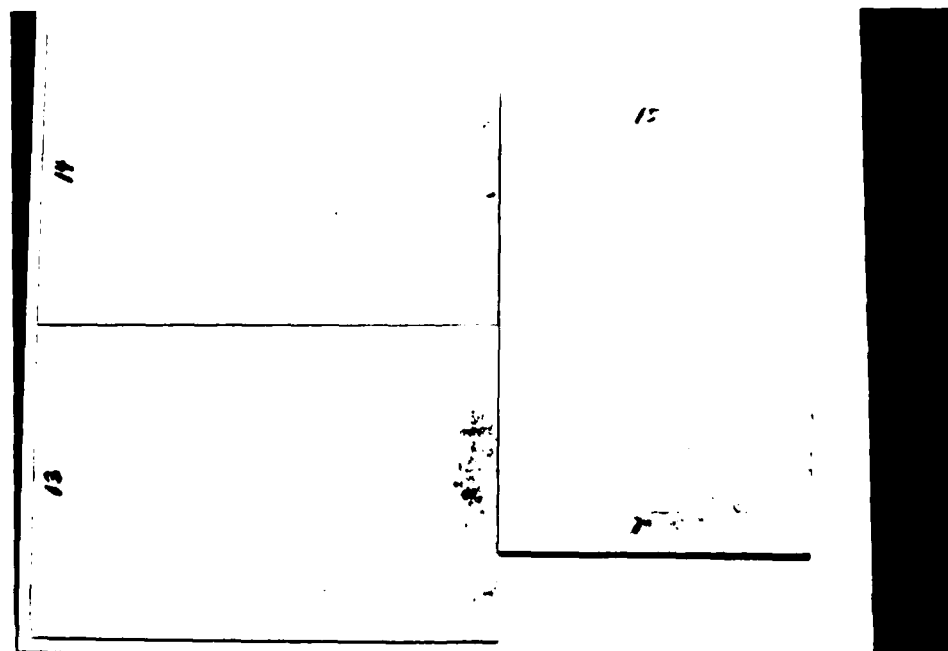
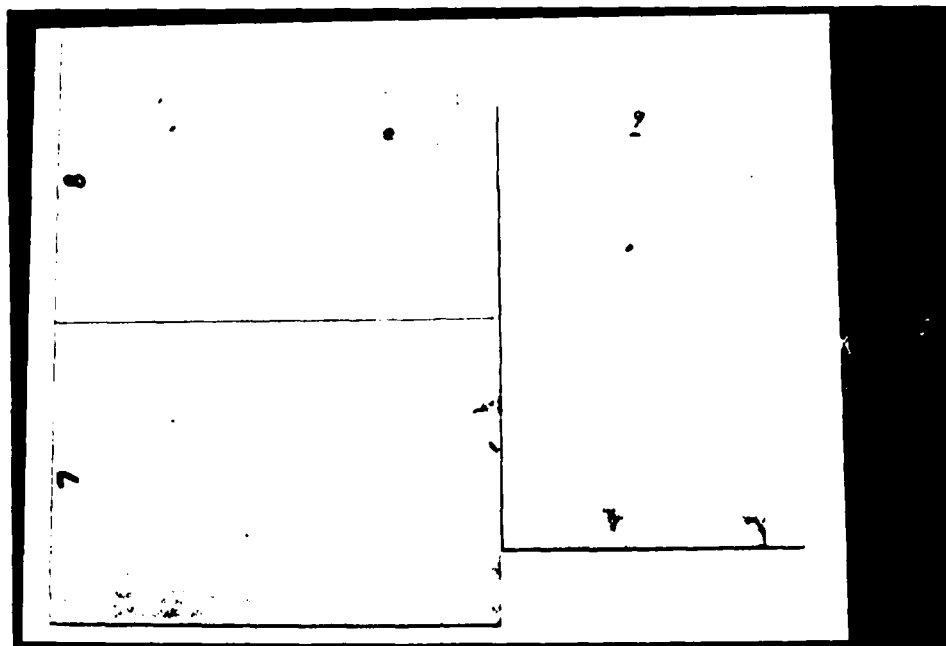


Figure 14. FPL 7075-T6 Al specimens exposed to standard NaCl salt fog environment, treated with (a) 100 ppm (pH 5) and (b) 1000 ppm (pH 4) adsorbed NTMP compound.

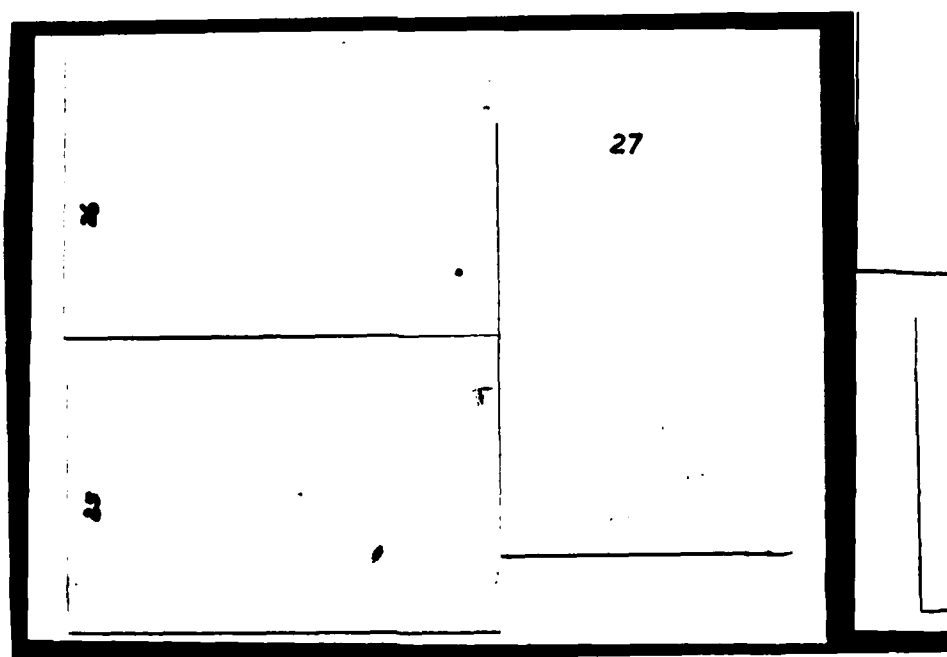
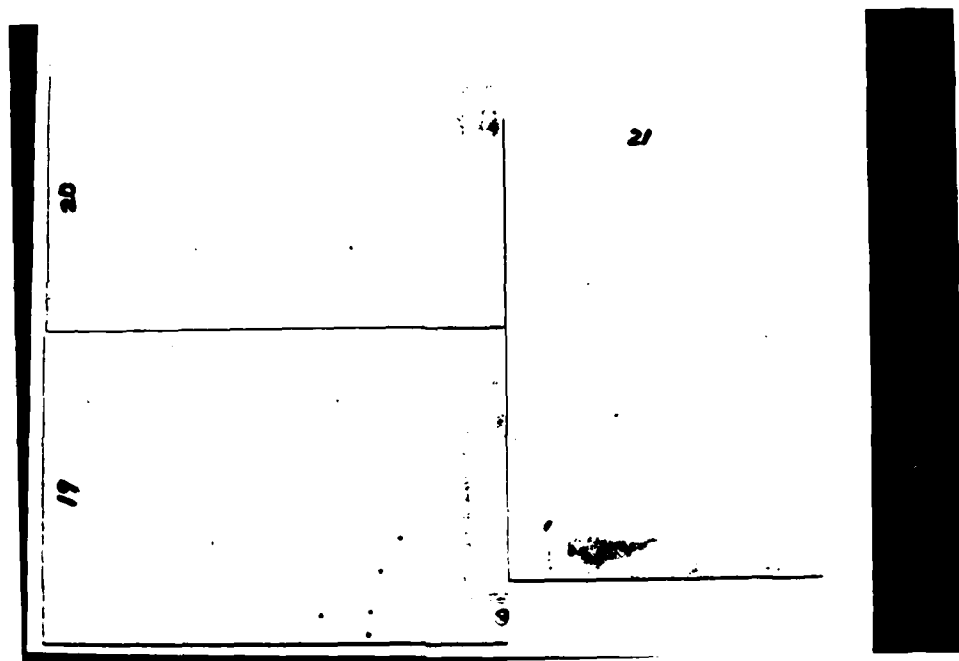


Figure 15. FPL 7075-T6 Al specimens exposed to standard NaCl salt fog environment, treated with (a) 1000 ppm (adsorbed) and (b) 5000 ppm (sprayed) M-8500 compound.

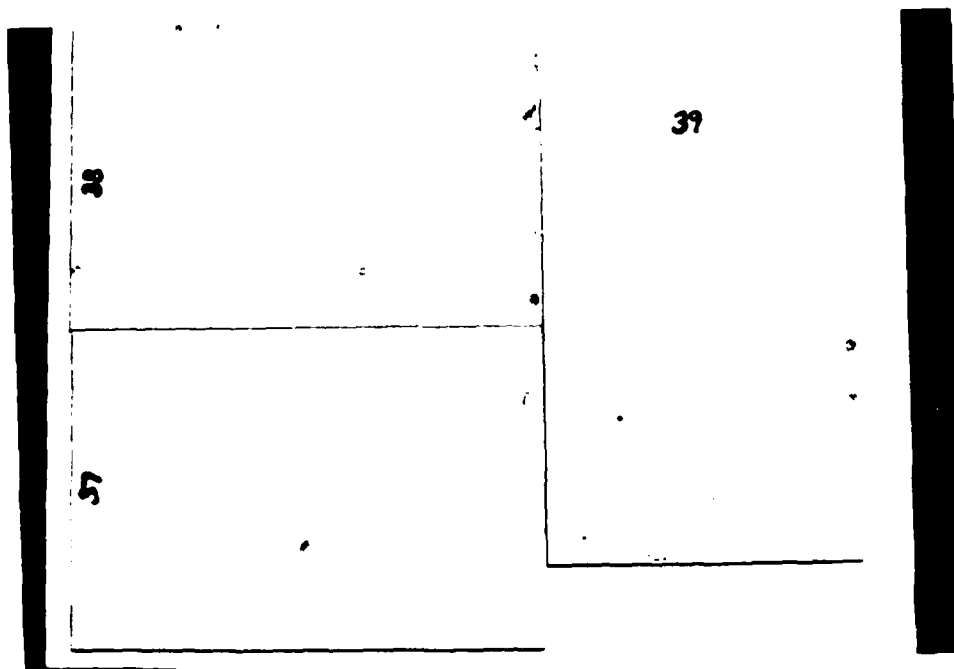
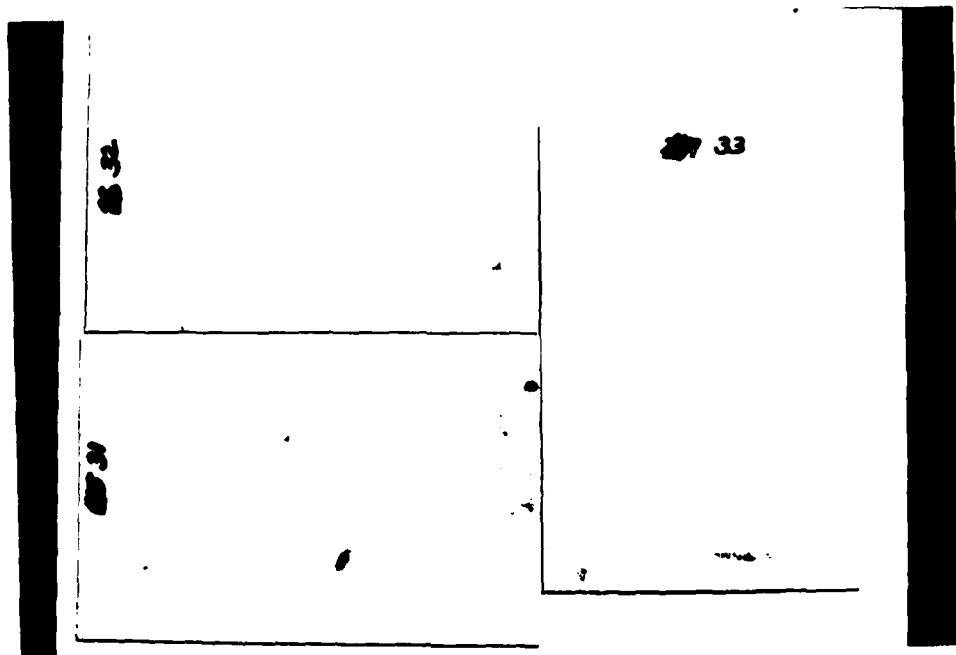


Figure 16. FPL 7075-T6 Al specimens exposed to NaCl salt fog environment, treated with (a) 5000 ppm G-n720 (sprayed) and (b) 5000 ppm DP 10 (sprayed) compounds.

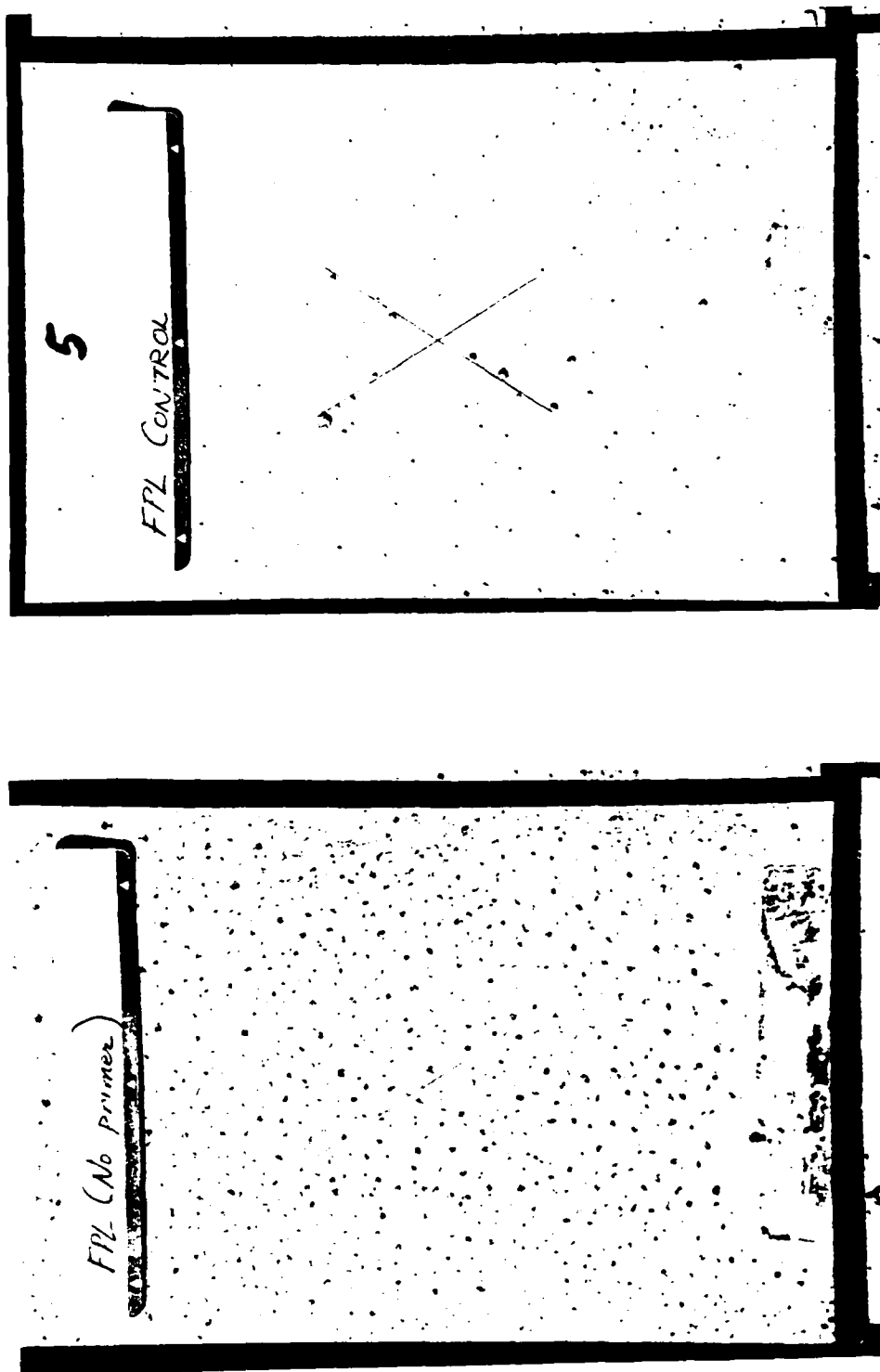


Figure 17. FPL 7075-T6 Al exposed to SO_2 salt fog; (a) untreated and (b) primed (unpigmented) control specimens.

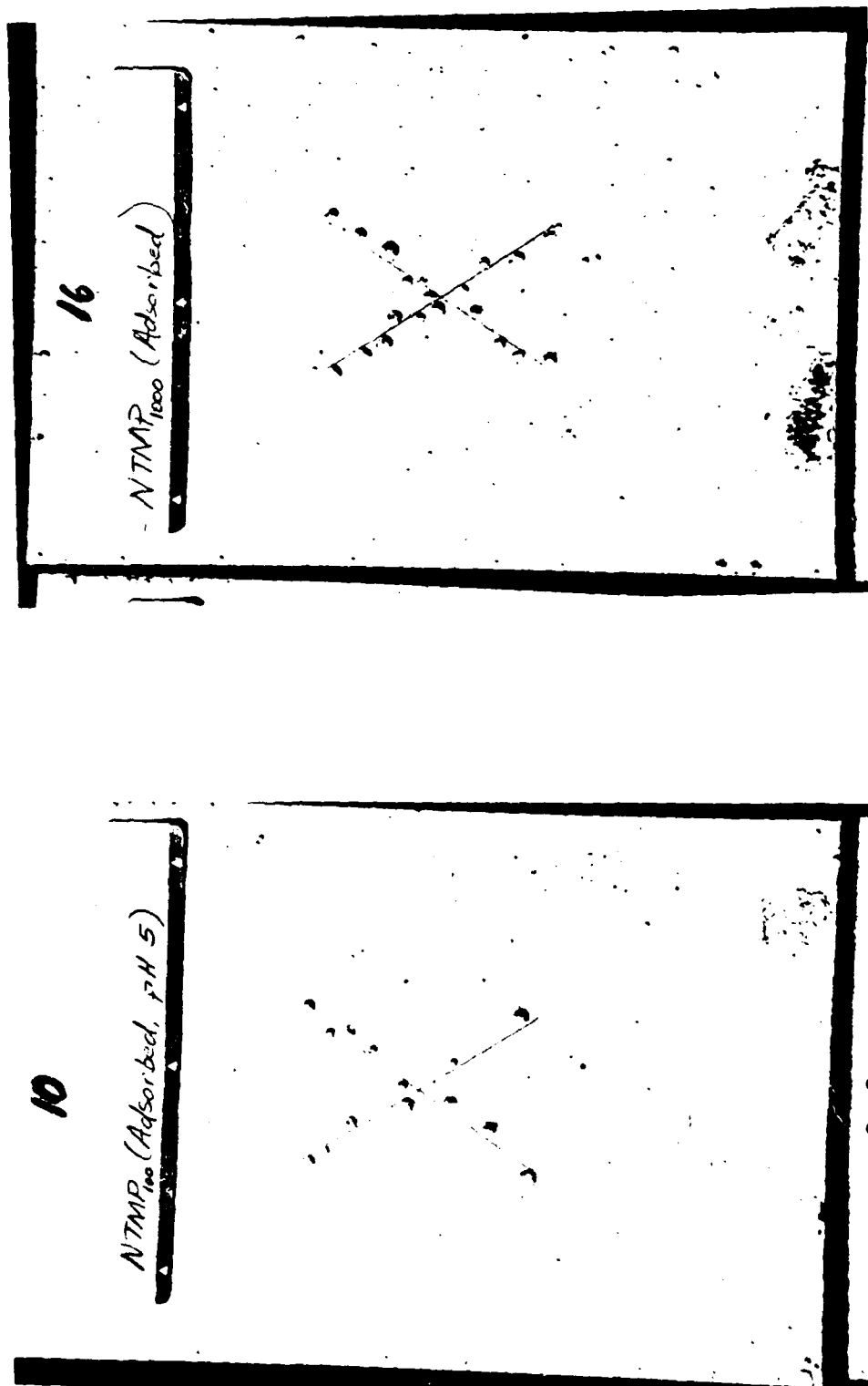


Figure 18. FPL 7075-T6 Al specimens exposed to SO_2 salt fog, treated with (a) 100 ppm (pH 5) and (b) 1000 ppm (pH 4) adsorbed NTMP compound.

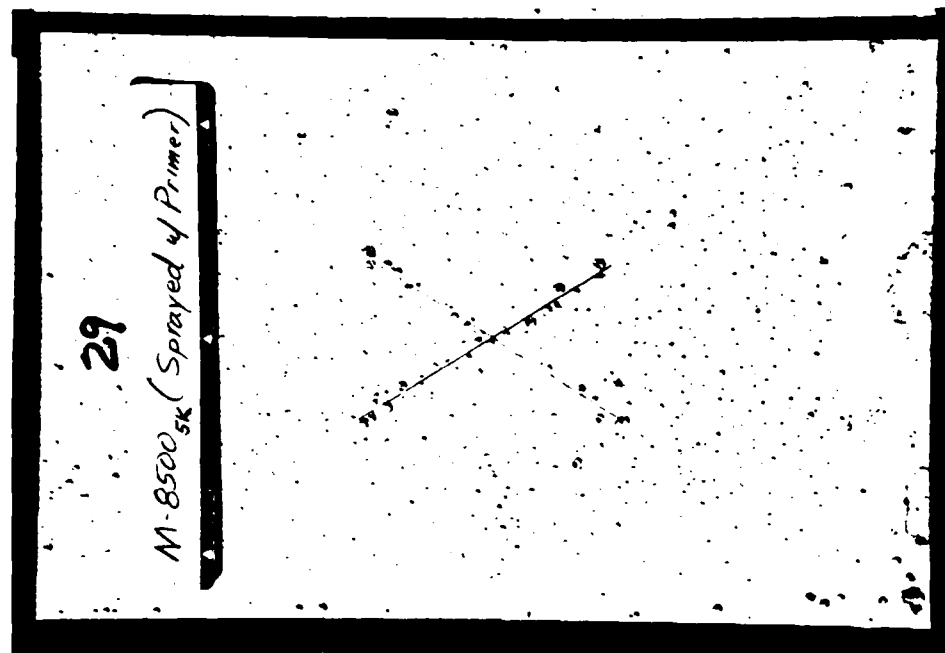
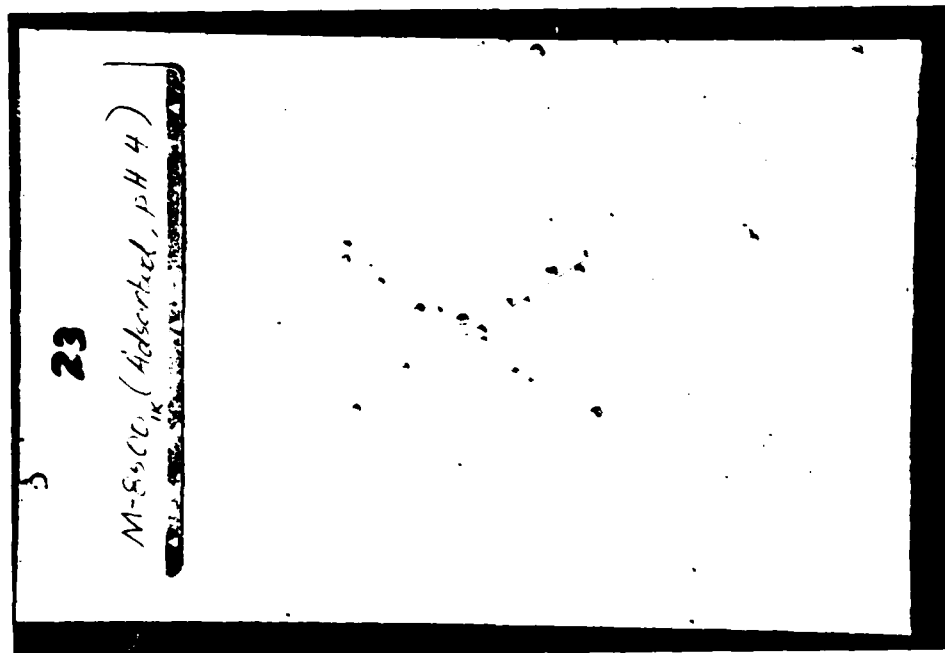


Figure 19. FPL 7075-T6 Al specimens exposed to SO₂ salt fog, treated with (a) 1000 ppm (adsorbed) and (b) 5000 ppm (sprayed) M-8500 compound.

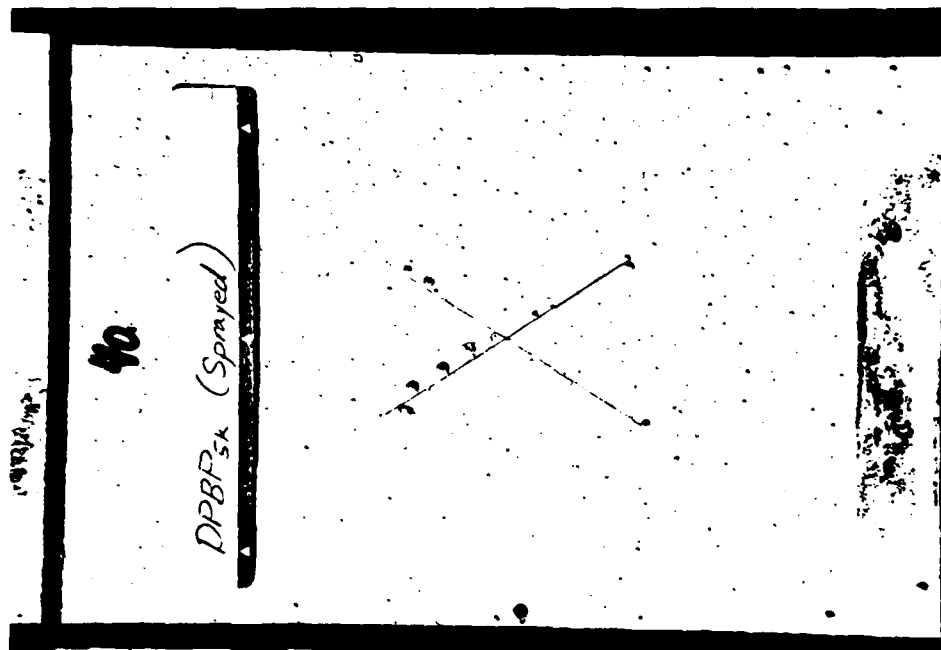
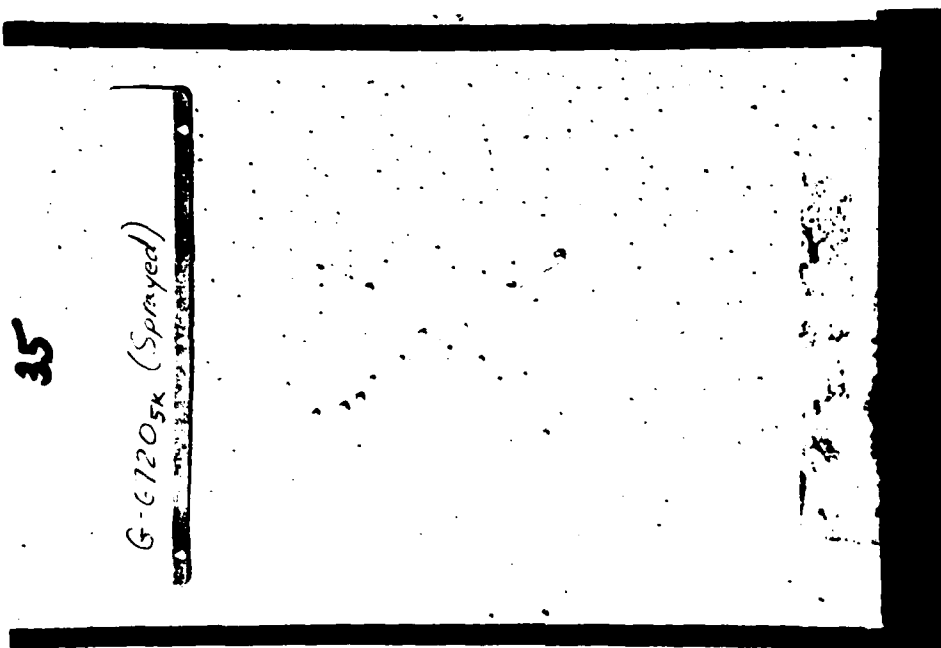


Figure 20. FPL 7075-T6 Al specimens exposed to SO_2 salt fog, treated with (a) 5000 ppm G-6720 (sprayed) and (b) 5000 ppm DPBP (sprayed) compounds.

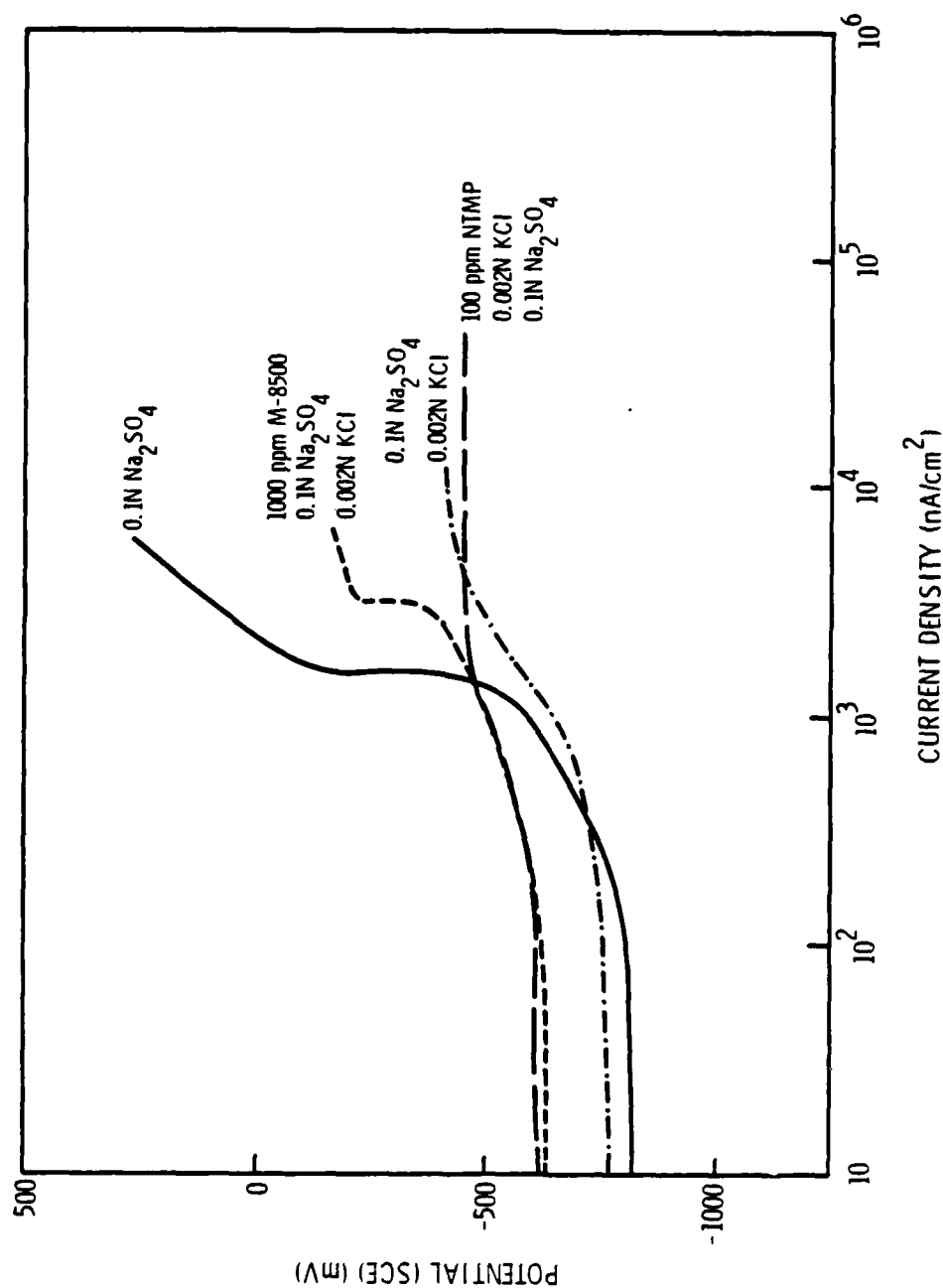


Figure 21. Electrochemical test results for two different inhibitor compounds in 0.1 N Na₂SO₄ electrolyte with added KC and inhibitors. The working electrode is polished 7075-T6 aluminum.

passivation. The addition of NTMP to the solution did not appear to protect the metal surface, when compared to the solutions containing no inhibitors. In contrast, the sample polarized in the electrolyte solution containing 1000 ppm mercaptopropyl silane (M-8500) did passivate up to -200 mV (SCE) and had a distinct pitting potential well above (more noble than) the potential where pitting initiates in NTMP-containing electrolytes. The alloy surface remained free from pits up to the -200 mV, above which small pits began to form.

IV. DISCUSSION

The corrosion resistance and polymer-bonding compatibility of the ionizable (acidic) organophosphonates and the neutral organosilanes are directly related to their inherent chemical properties. Specifically, NTMP inhibits the hydration of Al_2O_3 and maintains or improves bond durability with a nitrile-modified epoxy adhesive (depending on the surface treatment). The mercaptopropyl silane, in addition to having these properties, is also compatible with an epoxy-polyamide primer and resistant to localized environmental corrosion. These results are discussed in conjunction with the nature of the adsorbed films and the metal substrate surfaces.

The initial integrity of an adhesively-bonded system depends on the surface oxide porosity and microscopic roughness features resulting from the etching or anodization pretreatments.⁽⁴⁾ The thin FPL oxide⁽⁵⁾ provides a suitable substrate surface for evaluating some of the candidate inhibitors. The SAA surface characterized in this study consists of a thick ($9\text{ }\mu\text{m}$), porous, columnar layer that provides excellent corrosion resistance in both humid and aggressive (i.e., Cl^-) media due, in large part, to its thickness.

There are some interesting differences between the adsorption of ionizable (aminophosphate) and neutral (organosilane) compounds onto FPL- and SAA-prepared aluminum surfaces. The acidic NTMP species, consisting of quaternary $\equiv\text{N}^+$ and unprotonated $-\text{O}^-$ groups in solution,⁽⁶⁾ exhibits a pH-dependent multilayer adsorption maximum in an aqueous solution. At low solution concentrations ($\leq 100\text{ ppm}$), the coverage is essentially monolayer, corresponding to a P/Al ratio of 0.15.⁽⁷⁾ Wedge test results confirmed that this monolayer of NTMP leads to better long-term bond durability than multilayer films, which probably are formed by weak intermolecular hydrogen bonding and fail by a mixed-mode process.

The corrosion behavior of inhibitor-treated Al oxide systems provides clues to the mechanism of action for the phosphonates and silanes. In a purely hydrating environment, the hydrophilic NTMP provides short-term protection relative to untreated controls, probably by displacing H_2O in the oxide and forming a more stable complex.^(9,10) Used on SAA surfaces with the nitrile-modified epoxy adhesive, NTMP leads to a bond that fails only within the adhesive, i.e., cohesive failure. The FM 123-2 adhesive contains the curing agent, dicyanodiamide, which does not release low-molecular weight amines until temperatures are above $90^\circ C$.⁽¹¹⁾ The curing sequence and/or kinetics of this adhesive system may be important factors with respect to its compatibility with adsorbed NTMP. On the other hand, the epoxy-polyamide primer contains free amino groups at room temperature and may be inhibited by the electrophilic NTMP species prior to curing. Another example of curing inhibition in an acidic medium was observed when moderate amounts of salicylic acid were added to an epoxy-amine matrix system.⁽¹²⁾ Such behavior could be responsible for the weak bond strengths observed for the NTMP-containing oxide-primer specimens. In environments containing an aggressive species (e.g., Cl^-), the anion may interact with and become incorporated into the NTMP-oxide matrix, whereby it can attack the metal surface.

Silanes applied to an aluminum substrate can protect the surface from hydration.⁽¹³⁾ This hydration resistance was reflected by the wedge test performances of our silane-treated systems. Furthermore, electrochemical and salt fog results indicated that the oligomeric film maintained the resistance in environments containing aggressive species and oxidizing conditions. In contrast to NTMP, however, certain silanes are compatible and reactive with the epoxy polyamide primer as well as with the nitrile-modified adhesive which, in most cases, strengthens the oxide-epoxy bond. This result is presumably due to a chemical coupling of functional epoxide or mercapto side chains on the organosilane with the epoxy coatings during the curing process and indicates the true bifunctional nature of such inhibitors. The poor performance of the aminosilane compound (expected to strengthen the metal-

adhesive bond) is not completely understood at this time. Using similar concentrations, Walker⁽¹⁴⁾ has shown that some silanes are effective adhesion promoters for urethane and epoxy paints on aluminum and mild steel surfaces and significantly improve the initial, wet, and recovered bond strengths.

V. CONCLUSIONS

Ionic phosphonates, e.g., NTMP, are effective hydration inhibitors because they can form an insoluble complex with the oxide surface. They are useful as epoxy adhesive couplers in cases where the adhesive is compatible with the adsorbed phosphonate molecule.⁽⁹⁾ The wedge test results indicate that in both epoxy-aluminum systems studied, certain organosilanes (i.e., mercapto and epoxide derivatives) tend to both increase the epoxy-metal bond durability and maintain hydration resistance. The results of the salt fog and anodic polarization experiments further suggest that these silane films are effective against localized pitting.

With respect to adsorption conditions, NTMP exhibits a pH-dependent surface coverage, which includes a region characterized by a multilayer of hydrogen-bonded phosphonate molecules. These thick layers are weak and fail to provide good bond durability in a humid environment. However, NTMP monolayers are protective against hydration and are compatible with a nitrile-modified epoxy adhesive, although not with an epoxy-polyamide primer topcoat.

In contrast to NTMP, hydrolyzed silane compounds are adsorbed as oligomeric films, and confer corrosion resistance in both hydrating and certain aggressive ion, e.g., Cl^- , environments. These inhibitors can also couple with applied epoxy primer or adhesive formulations to further protect the metal against corrosion. The organosilanes do not appear to affect the curing process, e.g. % crosslinking, of the polymeric epoxy systems.

VI. REFERENCES

1. G.D. Davis, D.K. Shaffer and L.J. Matienzo, MML TR84-19c, End-of-First-Year Report under Contract No. 0019-82-c-0439, Martin Marietta Laboratories, Baltimore, Maryland.
2. G.D. Davis, D.K. Shaffer, L.J. Matienzo and J.S. Ahearn, J. Vac. Sci. Technol. A 3 (in press).
3. D.A. Hardwick, J.S. Ahearn and J.D. Venables, J. Mater. Sci. (in press).
4. J.D. Venables, J. Mater. Sci. 19, 2431 (1984).
5. J.D. Venables, D.K. McNamara, J.M. Chen and T.S. Sun, Appl. Surf. Sci. 3, 88 (1979).
6. R.P. Carter, M.M. Crutchfield and R.R. Irani, J. Inorg. Chem. 6, 943 (1967).
7. J.S. Ahearn, G.D. Davis, T.S. Sun and J.D. Venables in "Adhesion Aspects of Polymeric Coatings", edited by K.L. Mittal (Plenum, New York, 1983) p.281.
8. K.W. Allen, A.K. Hansrani and W.C. Wake, J. Adhes. 12, 199 (1981).
9. G.D. Davis, J.S. Ahearn, L.J. Matienzo and J.D. Venables, J. Mater. Sci. 20, 975 (1985).
10. F.I. Beliskii, L.B. Goryunova, P.V. Petrovskii, T.Y. Medved and M.I. Kabachnik, Akad. Nauk USSR 1, 103 (1982).
11. A.F. Lewis and R. Saxon in "Epoxy Resins: Chemistry and Technology," edited by C.A. May and Y. Tanaka (Marcel Dekker, New York, 1973) p. 413.
12. A.M. Ibrahim and J.C. Seferis, Polym. Compos. 6, 47 (1985).
13. F.J. Boerio, R.G. Dillingham, and R.C. Bozian, 39th Annual Conference, Reinforced Plastics/Composites Institute, The Society of the Plastics Industry, Inc., Sessions 4-A, 1 (January 1984).
14. P. Walker, J. Oil Colour Chem. Assoc. 65, 436 (1982).

END

10-86

DTIC